ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF BORON CONTAINING POLY(METHYL METHACRYLATE) BY ATRP

M.Sc. THESIS

Selcan CELİOĞLU

Department of Polymer Science and Technology

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Thesis Advisor: Prof. Dr. İ. Ersin SERHATLI

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ATRP İLE BOR İÇEREN POLİMETİLMETAKRİLAT SENTEZİ

YÜKSEK LİSANS TEZİ

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Tez Danışmanı: Prof. Dr. İ. Ersin SERHATLI

ARALIK 2016

Selcan CELİOĞLU, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **515141020**, successfully defended the **thesis** entitled "**SYNTHESIS OF BORON CONTAINING POLY(METHYL METHACRYLATE) BY ATRP**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. İ. Ersin SERHATLI** **İstanbul Technical University**	.....
Jury Members :	**Prof. Dr. İ. Ersin SERHATLI** **İstanbul Technical University**	.....
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	Prof. Dr. Tarık EREN **Yıldız Technical University**	.....

Date of Submission : 30 November 2016
Date of Defense : 22 December 2016

To my family,

FOREWORD

This study has been carried out in POLMAG Laboratory (Polymeric Materials Research Group), Faculty of Science and Letters, Istanbul Technical University.

First of all, I would like to gratefully and sincerely thank to my advisor, Prof. Dr.I.Ersin SERHATLI for offering, knowledge and experience.

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December 2016 Selcan CELİOĞLU
(Chemist)

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ABBREVIATIONS

ATRP : Atom Transfer Radical Polymerization
CBD : Carboranediol
CBM : Carboranemonool
CBD-Br : Carboranediol with bromide groups
CBM-Br : Carboranemonool with bromide groups
DSC : Differential scaning calorimetry
DCM : Dichloromethane
FT-IR : Fourier transform infrared spectroscopy
GPC : Gel permeation chromatography
^{1}H-NMR : Proton nuclear magnetic resonance
^{11}B-NMR : Boron nuclear magnetic resonance
M_w : Molecular weight
MMA : Methyl methacrylate
µL : Microliter
PDI : Polydispersity indeks
PMMA : Poly(methyl methacrylate)
TGA : Thermogravimetric analysis
THF : Tetrahydrofuran

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SYNTHESIS OF BORONE CONTAINING POLY(METHYL METHACRYLATE) BY ATRP

SUMMARY

Carborane divided into three groups according to the cage shape these are closo, nido and arachno. Closo carborane can be classify into three isomers according to carbon atoms positions, orto, meta and para. O-Carborane ($C_2B_{10}H_{12}$) is a cage structure which content boron (^{11}B), hydrojen (^{1}H) carbon (^{12}C) atoms. As a result of the research have been demonstrated to show a variety of physical and chemical effects due to the content of boron in the polymer.In recent years,the use of boron in the polymer has increased due to the flame retardent thermal properties. There has been many using area for O-carborane compound from increasing flammability to medical applications.In this study Atom Transfer Radical Polymerization method was used which is type of controlled polymerization. Many type of vinyl monomers can polymerized with ATRP method especially styrene, acrylates and methacrylates. Different ATRP conditions are used for different monomer types.

In this study first of all two different initiators were created and then these two initiators were used in ATRP reaction effectively. Hydroxyl groups were changed with active bromide group with the help of . 2-bromopropionyl bromide that are take part in Carboranemonool and carboranediol structures. Reaction yield were calculated gravimetrically as 55.4% and 54.8%. FT-IR and NMR methods were used for characterization of initiators.Carborane initiators were used for polymerization of methylmethacrylate.Mainly the effect of reaction time was examined onto the polymerization.

For the monofunctional initiator carboranemonool, methylmethacrylate, copper(I) bromide and PMDETA was polymerized in 15,45,60,90,180 minutes. For the bifunctional initiator carboranediol, methylmethacrylate, copper(I) bromide and PMDETA was polymerized in 5,7,8,15 hours.One control pMMA were synthesized 2 hours to compare with all polymers. Conversions of polymers were determined gravimetrically.Gel permeation chromotography (GPC) was used to determine molecular weight of all polymers,Differential scanning calorimetry (DSC),were used to determine Tg values of all polymers Thermogravimetric analyser (TGA) were used to determine 50% percent degradation time and char yield amount of polymers at 500 ^{o}C and 800 ^{o}C.These methods were used for characterization of all polymers.

ATRP İLE BOR İÇEREN POLİMETİLMETAKRİLAT SENTEZİ

ÖZET

Karboranlar ($C_2B_{10}H_{12}$) bor (^{11}B), hidrojen (^{1}H) ve karbon (^{12}C) atomlarından oluşan bir kafes yapısına sahiptirler.Kafes yapılarının çeşitliliklerine göre 3 tip karboran vardır bunlar kloso, nido ve arakno olarak adlandırılırlar. Kloso karboran çeşidi de kendi içerisinde karbon atomlarının pozisyonlarına göre 3 farklı izomer tipine sahiptir. Bu izomer tipleri Orto, meta ve para şeklindedir. Polihedral heteroboranlar 40 yılı aşkın süredir araştırma konusu olarak çalışılmaktadır. Bu bileşikler fiziksel ve kimyasal özelliklerinden dolayı; katalizör, radyofarmasötik, polimer, tekli koordinasyon bileşiklerinin hazırlanması gibi alanlarda kullanılmaktadır.

Bu çalışmada temel olarak o-karboran tipi kullanılmıştır. Bor elementinin yapısı gereği, yapılan araştırmalar sonucunda polimerlerde çeşitli fiziksel ve kimyasal etki gösterdiği ortaya konmuştur. Özellikle yanmazlık arttırıcı termal özelliklerinden dolayı bor elementinin polimerlerde kullanımı son yıllarda artış göstermiştir. O-karboran bileşiğinin yanmazlık arttırıcı özelliğinden medikal uygulamalara kadar birçok kullanım alanı mevcuttur. Geleneksel radikal polimerizasyon yöntemleri ile dar molekül ağırlığı dağılımı ve iyi tanımlanma gibi polimerlerin özelliklerini etkileyen faktörleri kontrol etmek zordur. Son yıllarda yaygın bir şekilde geliştirilen kontrollü/yaşayan radikal polimerizasyon (CLRP) tasarlanmış yapılı ve dar bir molekül ağırlığı dağılımına sahip polimerlerin sentezlenmesi için etkili bir yöntem temin etmektedir. Atom transfer radikal polimerizasyonu (ATRP), kararlı serbest radikal polimerizasyoun (SFRP), nitroksit aracılı radikal polimerzasyon (NMRP) ve tersinir eklenme-parçalanma zincir transfer polimerizasyonu (RAFT), CLRP tekniklerine örnek olarak gösterileblir. Bu teknikler arasından metal katalizörlü yaşayan radikal polimerizasyonu, daha çok bilinen adı ile atom transfer radikal polimerizasyonu (ATRP), değişik topolojilerde doğrusal polimerler ve kopolimerler elde etmek için kullanılan en etkin kontrollü / "yaşayan" polimerizasyon metodu haline gelmiştir. Bu tekniğin temeli monomerik ya da polimerik halojenur molekülünden metal kompleksine halojen atomu transferi yapılmasına dayanır. Bu transfer sırasında organik bir radikal ve yüksek oksidasyon seviyesinde geçiş metali kompleksi oluşturulur. Yüksek oksidasyon seviyesindeki metal ligand çifti ile düşük oksidasyon seviyesindeki metal ligand çiftinin reaksiyon dengesi düşük oksidasyon seviyesi yönündedir. Bundan dolayı, radikal konsantrasyonu hep düşük seviyede

tutularak sonlanma reaksiyonları azaltılır ve monomerin polimerleşmesi kontrol altına alınır. Katalizör-ligand kompleksi ATRP de zincir büyümesi kontrolünde, polimerizasyon hızında ve molekül ağırlığı dağılımında anahtar rol oynamaktadır. ATRP mekanizması içinde kullanılan monomer ve istenen reaktiviteye göre birçok farklı ligand kullanılabilir. En çok kullanılanları ise PMe6TREN (Tris-[2-dimetil aminoetil]amin) ve TPMA (tris[(2-piridil)metil]amin)'dir; çünkü bu ligandlar ile yüksek bağlanma ve ayrışma hızları ile yüksek reaksiyon hızı elde edilir. Başlatıcı olarak alkil bromid gibi organik halidler kullanılabilir. Katalizör seçimi ise kontrollü büyüme için çok önemlidir. Çünkü katalizör ATRP mekanizması içindeki tepkimelerin dengesini sağlayan en büyük etmendir. Uyumlu, ucuz olması ve verimliliği sebebiyle bakır içeren katalizörlerin kullanımı yaygındır. Atom transfer radikal polimerizasyonu için genellikle bakır tabanlı katalizörler kullanılır ve bu katalizörler için bipiridin ve çok dişli aminler kullanılır. Bu çalışmada bir kontrollü polimerizasyon türü olan Atom Transfer Radikal Polimerizasyonu (ATRP) yöntemi kullanılmıştır. Atom Transfer Radikal Polimerizasyonu (ATRP) monomer, transfer edilebilir (psödo) halojene sahip başlatıcı ve her hangi bir ligand ile uyumlu geçiş metal komplesinin oluşturduğu bir katalizörü içeren çoklu bileşenli bir sistem olup en ilgi çekici olan kontrollü yaşayan polimerizasyon methodlarından biridir. ATRP'de büyüyen radikaller geçiş metal kompleksi ile halojenli türlerin değişimi ile sağlanan dinamik denge sayesinde tersinir olarak aktive ve deaktive edilebilir. ATRP ile başarılı bir polimerleşme gerçekleştirmek için çözücü ve sıcaklık da dikkate alınması gereken parametrelerdendir. Atom Transfer Radikal Polimerizasyonu (ATRP) tahmini molekül ağırlığı, dar düşük molekül ağırlığı dağılımı, çok değişken zincir uç fonksiyonalitesi ve kontrol edilebilen molekül yapısı üzerine etkin kontrol sağlayan en etkili kontrollü radikal polimerizasyonlarından biridir.

ATRP' de kullanılan özel Cu(I), Co, Rh, Fe, …/Ligand sistemi sayesinde katalizlenen bu metotta monomerler büyüyen polimer zincirine eklenebilir. Bu denge organik halojen ile Cu(I) tuzları gibi geçiş metali arasındaki redoks reaksiyonu üzerinden karbon-halojen bağının tersinir homolitik bölünmesini içerir. ATRP'den önce ortaya çıkan kontrollü polimerleşme yöntemlerinde her türlü monomer kullanılamamasına karşın, ATRP mekanizması ile geniş bir monomer seçkisi polimerleşme için kullanılabilir. ATRP yönteminin kullanılabildiği monomer tipleri genellikle büyüyen radikali kararlı hale getirebilen ve aynı zamanda fonksiyonel gruplara sahip olan monomerlerdir. Bir çok vinil monomeri ATRP yöntemi ile polimerleştirilebilir ve en çok kullanılanlar; stiren, akrilatlar, akrilonitril, izopren, akrilamid ve metakrilat monomerleridir. Herbir monomer tipi için farklı ATRP koşulları kullanılmaktadır.

Bu çalışmada metilmetakrilat monomerinin polimerleştirilmesinde kullanılabilecek farklı iki radikal başlatıcı sentezlenmiştir ve sentezlenen bu iki başlatıcı ATRP reaksiyonunda etkin bir şekilde kullanılmıştır. İlk olarak karboranmonool ve karborandiol yapılarındaki hidroksil (OH) uç grupları 2-bromopropiyonil bromür maddesi ve çözücü olarak kloroform kullanılarak modifiye edilmiş ve uç gruplarda aktif brom grubu olması sağlanarak CBM-Br ve CBD-Br başlatıcı grupları sentezlenmiştir. Reaksiyonların verimi gravimetrik olarak hesaplanarak %55.4 ve

%54.8 olarak bulunmuştur. Yeni oluşan yapılar farklar FT-IR ve NMR yöntemleri kullanılarak incelenmiştir. İncelemeler sonucunda hidroksil fonksiyonlarının brom uç gruplarıyla değiştirildiği ispatlanmıştır. Sentezlenen karboran yapıları metilmetakrilat monomerinin atom transfer radikal polimerizasyon yöntemi ile polimerleşmesinde başlatıcı olarak kullanılmıştır.

Yapılan çalışmalarda temel olarak reaksiyon süresinin polimerizasyona etkisi incelenmiştir. Metilmetakrilat monomeri carboranlar ile birliktebakır(I) bromür */N,N,N′,N′,N″*-pentametildietilentriamin katalizörlüğünde karboranmonool-bromür (CBM-Br) için 15, 45, 60, 90, 180 dakika olarak ve karborandiol-bromür (CBD-Br) için 5, 7, 8, 15 saat süresince reaksiyon vermesi sağlanmıştır. Sentezlenen polimer çözeltileri üzerine tetrahidrofuran çözücüsü eklenerek kısa alümina kolondan geçirilmiştir(kolon içerisinde nötral alumina kullanılmıştır) ve bu sayede ortamda kalan fazla bakır uzaklaştırılmıştır. Bir sonraki aşamada ise solvent (tetrahidrofuran) rotary cihazı ile uçurularak sentezlenen polimerler bir miktar metanol içerisinde çöktürülerek süzülmüştür ve oluşan polimerler toplanarak reaksiyon verimleri hesaplanmıştır. Diğer bir yandan ise ethyl-2-bromoisobutyrate başlatıcısı ile 2 saat süren bir polimerizasyon reaksiyonu yapılmıştır kullanılan başlatıcı tipi ve reaksiyon süresi hariç diğer tüm şartlar başlatıcı olarak karboran kullanılan polimerizasyon reaksiyon koşulları ile aynıdır.Bu şekilde sentezlenen kontrol polimeri sayesinde çeşitli karşılaştırmalar yapılabilmiştir. Elde edilen polimerlerin molekül ağırlıkları (Mn) ve molekül ağırlık dağılımları (Mw) jel geçirgenlik kromotografisi (GPC) ile incelenmiştir. Polimerizasyonların reaksiyon sürelerinin artışına bağlı olarak sentezlenen polimerlerin molekül ağırlıklarının da arttığı gözlemlenmiş ve bununla birlikte molekül ağırlık dağılımının (PDI) düştüğü gözlemlenmiştir.Yine GPC analiz sonucunda ek olarak ikinci bir polimer piklerine rastlanmamış ve böylece metilmetakrilat monomerinin hiçbir homopolimer oluşturmadığı tespit edilebilmiştir. Sentezlenen polimerlerin kimyasal yapıları FT-IR, ^{1}H-NMR ve ^{11}B-NMR yöntemleri ile incelenmiş ve karşılaştırılmıştır. Başlatıcıların ve sentezlenen polimerlerin Bor nmr sonuçları karşılaştırıldığında Bor nmr pikleri başlatıcılar için daha keskin ve dar pikler olup, polimerlerin bor nmr pikleri ise daha geniş ve yayvan olarak gözlemlenmiştir. Hidrojen nmr sonuçlarında ise polimer yapısında gelen temel olarak metilmetakrilat pikleri gözlemlenmiş ve polimerizasyonun gerçekleştiği ispatlanmıştır. Sentezlenen polimerlerin termal özelliklerini incelemek için ise DSC ve TGA cihazları ile kullanılmıştır. DSC cihazı ile sentezlenen polimerlerin Tg değerleri belirlenmiştir. TGA cihazı ise polimerlerin %50 bozunma sıcaklıkları ve 500 ^{o}C ve 800 ^{o}C deki kalan madde miktarları hesaplanmıştır. Karboranmonool başlatıcısı kullanılarak sentezlenen polimerlerin karborandiol başlatıcısı kullanılarak sentezlenen polimere oranla daha kısa sürede polimerleştiği gözlenmiştir.Termal özellikleri karşılaştırıldığında ise karborandiol kullanılarak sentezlenen polimerlerin %50 bozunma sıcaklıklarındaki artış dikkat çekerken karboranmonool ile sentezlenen polimerlerin %50 bozunma sıcaklıklarında ise düşüş tespit edilmiştir.

1. INTRODUCTION

Boron is one of the most non-metalic element in periodic table which is locatedn into IIIA group.It is composed of two stable isotopes, their mass numbers are 10 and 11. It is very hardness like a diamond, melting point of boron at 2300 ^{o}C [1].

O-Carborane ($C_2B_{10}H_{12}$) is a cage structure which content boron (^{11}B), hydrojen (^{1}H) carbon (^{12}C) atoms. As a result of the research have been demonstrated to show a variety of physical and chemical effects due to the content of boron in the polymer. In recent years, the use of boron in the polymer has increased due to the flame retardent thermal properties [2]. There has been many using area for O-carborane compound from increasing flammability to medical applications [3]. Atom transfer radical polymerization (ATRP) is one of the most effective methods to control radical polymerization. The end groups of the polymers are defined by the structure of the initiator used. The alkyl group of the alkyl halide initiator remainsat one end of the produced polymer chain, a halogen atom is quantitatively transferred to the other end of the chain [4].

It is not possible to synthesis the polymer with narrow molecular weight distribution and good structure by conventional radical polymerization method. Controlled/living radical polymerization (CRP) has been developed in past the few years. CRP is an efficient way of synthesizing polymers with designed structure and narrow moleculer weight distribution. Thanks to the (ATRP) which is one of the most investigated CRP, well-defined structure can provided by using suitable initiators [5,6].

In this thesis will about to polymerize methyl methacrylate by ATRP as using brominated o-carboranemonool and o-carboranediol as initiator. In this reason, -OH end group are brominated to create bromine reactive groups. This functional group take part in initiating the pMMA chain growth.For charactarization of all polymers; FT-IR, ^{1}H-NMR, ^{11}B-NMR, DSC and TGA analysis method was used.

2. THEOROTICAL PART

2.1 History of Carborane

Carboranes ("carbaboranes" in the formal nomenclature) are polyhedral boron carbon atomic groups that are balanced out by electron-delocalized covalent bonding in the skeletal structure**.** As opposed to established organoboranes, for example, borabenzene (C_5H_5B), the skeletal carbon atoms in carboranes commonly have no less than three and upwards of five or six neighbors in the bunch, framing stable—at times, exceedingly steady—atomic structures. Until the mid-1950s, Carboranes have been known. But for much of that time they were of interest primarily to boron chemists, theoreticians interested in their structures and bonding, and small groups of industrial researchers, who recognized their potential for creating extremely heat-stable polymers. In recent years, Carborane chemistry is developed in medicine, nanoscale engineering, catalysis, metal recovery from radioactive waste, and a number of other areas.The first carborane was discovered and characterized (though not the first to be reported in the open journals), 1,2-$C_2B_{10}H_{12}$ (closo-1,2-dicarbadodecaborane [7] or trivially ortho-carborane) is still, more than a half-century later, the most widely utilized member of its genre and is commercially available. Many derivatives of o-carborane were synthesized to order for a variety of applications [8].

2.2 *O*- Carboranes (Closo-1,2-dicarbadodecaboranes)

$C_2B_{10}H_{12}$ (closo-1,2-dicarbadodecaborane has three isomer types; These are ortho(1), metha(2), para(3). Types of isomers are different from each other according to carbon atoms positions. Isomers types and IUPAC names of carboranes can be seen at Figure 2.1 [9].

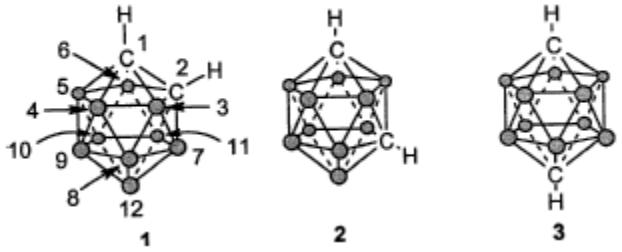


Figure 2.1: Ortho(1), meta(2), para(3) carborane.

In the cluster structure, each of carbon and boron atoms have approximetly icosahedral geometry hekzakoord.

O- Carboranes were synthesized by two groups in 1963 [9,10]. In generally *O*-Carboranes ($B_{10}H_{12}L_{2)}$ are obtained reaction which has a weak base(L= CH_3CN, RSR, R_3N)and decaborane ($B_{10}H_{14}$) both mono and disubstituted alkines [11,12].

The reactions are usually obtained by boiling under reflux for several hours (6-24 h) in acetonitrile or toluene.Reaction of the acetylene and compound with B10H12L2; can be occurred in the presence of esters, halides, carbamates, ethers and nitro groups which contain functional groups. But these reactions can not be occurred in the presence of nucleophilic species such as ; alcohol, acid or amines [13]. Synthesis of carboranes can be seen (Figure 2.2) [11].

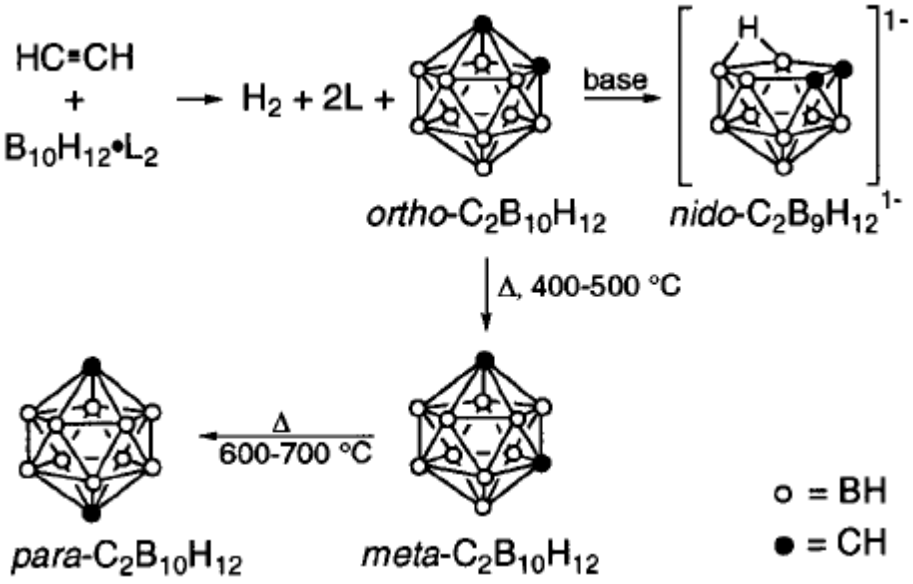


Figure 2.2: Synthesis of carboranes.

Meta-, and para-carborane isomers can be prepared as a result of thermal isomerization of *ortho*-carborane under an inert atmosphere. *ortho*-carborane can return to meta- isomer in 400-500 ^{o}C and meta- isomer can be rearrangement para-isomer between 600-700 ^{o}C (Figure 2.2). Mechanism of isomerization were researched intensely [14-16] and three decaboranes isomers can be widely used for commercial sources.

2.3 Application of Carboranes

Thanks to the physical and chemical properties of carboranes that are used for preparation of catalyst, [17,18], radiopharmaceuticals [19], polymer [20,21] and single coordination compound [22,23]. Also thanks to the chemical structures ,carboranes are used in canser treatment method which is boron neutron capture therapy (BNCT).

For improve carborane-containing polymers, carborane structure is mostly used due to contains highly boron and great thermal and chemical stabilitiy. The thermal stability of polymers could be greatly enhanced by the incorporation of carboranes into the matrices [24-28].

2.4 Controlled/Living Free Polymerization

Preparing high molecular weight polymers is most important feature of Free Radical polymerization (FRP). Because many vinyl monomers under mild conditions can be used, requiring the absence of oxygen but tolerant to water, and large temperature ranges (-20 to 200 ^{o}C). Moreover most of monomers can easily copolymerize radically leading to an infinite numbers of copolymers with properties dependent on the proportions of the comonomers. FRP with a thermal initiator can be separated into three essential steps, initiator decomposition and initiation, propagation, and termination by combination or disproportionation.These three steps were summerized in Figure 2.3 [29].

Initiator dissociation	$I \overset{k_d}{\rightarrow} 2R\cdot$
Initiation	$R\cdot + M \overset{k_i}{\rightarrow} P_1\cdot$
Propagation	$P_n\cdot + M \overset{k_p}{\rightarrow} P_{n+1}\cdot$
Termination by combination	$P_n\cdot + P_m\cdot \overset{k_{tc}}{\rightarrow} D_{n+m}$
Termination by disproportionation	$P_n\cdot + P_m\cdot \overset{k_{td}}{\rightarrow} D_n + D_m$

Figure 2.3: General mechanism of free radical polymerization.

The poor control of macromolecular structures including degrees of polymerization, polydispersity index, and also the practical impossibility to synthesize block copolymers, and other advanced structures are the some disadvantages of traditional radical polymerization. Various processes have been developed during the last decade for the control of free radical polymerization (CRP) Thanks to the development ; new ways of synthesizing polymers with low polydispersities, new architectures, compositions, functionalities and molecular composites (Figure 2.4) [30,60].

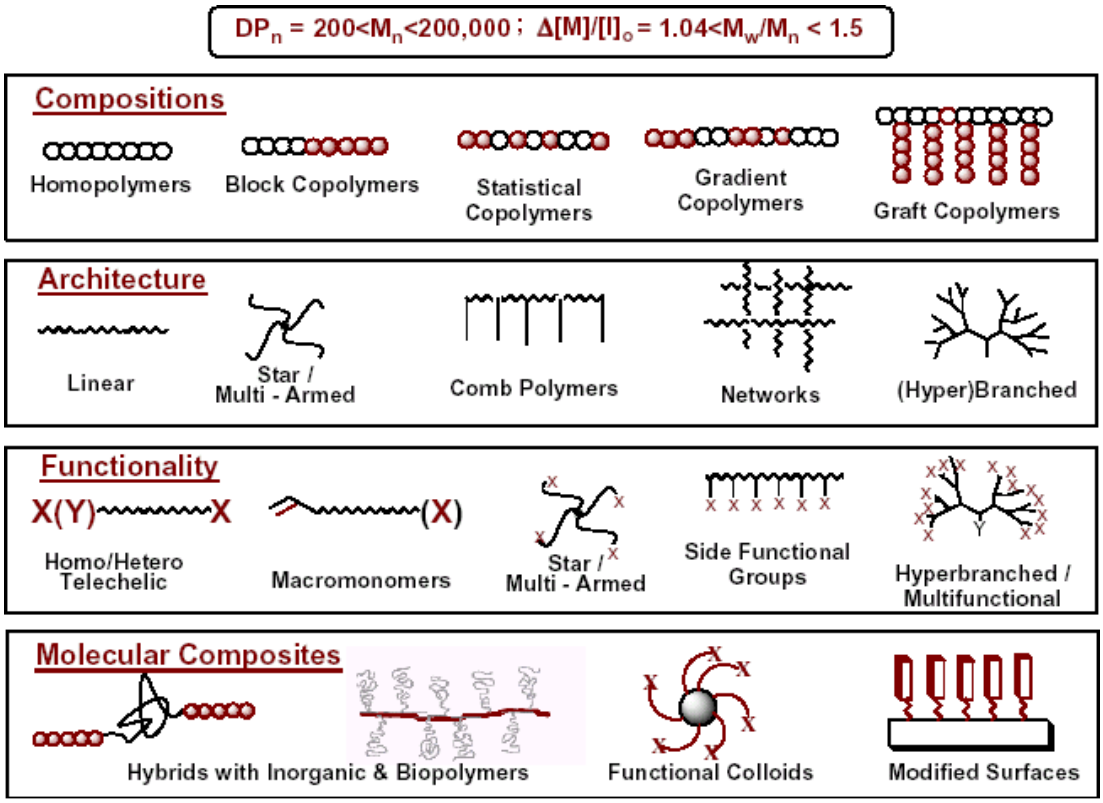


Figure 2.4: Products of controlled free radical polymerization.

2.5 Classification of CRPs

CRP is seperated into many categories, depending on the chemistry of exchange and structure of the dormant species.Mechanistically, CRPs can bereversible addition fragmentation transfer (RAFT), stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and nitroxide mediated polymerization (NMP). All of these methods are based on establishing a 25 rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of the dormant species. The dormant chains may be alkyl halides, as in atom transfer radical polymerization (ATRP) or degenerative transfer (DT), thioesters, as in reversible addition fragmentation chain transfer processes (RAFT), alkoxyamines, as in nitroxide mediated polymerization (NMP) or stable free radical polymerization (SFRP), and potentially even orgonometallic species. Free radicals may be generated by the spontaneous thermal process (NMP, SFRP) via a catalyzed reaction (ATRP) or reversibly via the degenerative exchange process with dormantspecies (DT, RAFT) [31].

2.6. Atom Transfer Radical Polymerization (ATRP)

In 1995, ATRP was developed independently by Matyjaszewski and Sawamoto [32]. that used a simple, inexpensive polymerization system [33, 34]. The name atom transfer radical polymerization originates from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP has its roots in atom transfer radical addition (ATRA), that targets the formation of 1:1 adducts of alkyl halides and alkenes, also catalyzed by transition metal complexes. Copper (I) complex under goes a one-electron oxidation with corresponding abstraction of a halogen atom from a beginning compound in ATRA Figure 2.5. Organic radical and a copper (II) complex are generated by this reaction and substituents on the organic halide can facilitate the reaction by stabilizing the resulting radical. The organic radical can then add to an unsaturated group in an inter- or intramolecular fashion and then reabstract a halogen atom from the copper (II) complex to reform the original copper (I) complex and to form the product.Because of the copper (II) complex act as a persistent radical and controls the concentration of the intermediate radicals, compounds derived from the self-reaction of radicals (i.e.,termination) contain very little of the product. Substrates are typically chosen such that if addition occurs, then the newly formed radical is much less stabilized than the initial radical and will essentially react irreversibly with the copper (II) complex to form an inactive alkyl halide product (kact>>k'act) for this reaction. Therefore, usually only one addition step occurs in ATRA; nonetheless, provided that starting and product alkyl halides possess similar reactivities toward atom transfer, then it should be possible to repeat the catalytic cycle and add multiple unsaturated groups as in a polymerization reaction [35].

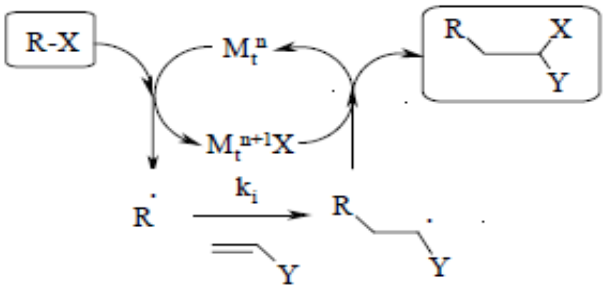


Figure 2.5: Mechanism of ATRA.

2.6.1 Mechanism of ATRP

One of the most versatile controlled radical polymerization method is atom transfer radical polymerization. ATRP method utilizes a reversible halogen atom abstraction step in which a lower oxidation state metal (M_t^n complexed by ligands LGN) reacts with an alkylhalide (P_n-X) to make a radical ($P_n^{\bullet}$) and a higher oxidation state metal complex ($XM_t^{n+1}LGN,k_a$). Then this radical adds monomer to generate the polymer chain (k_p). The higher oxidation state metal can then deactivate the growing radical to generate a dormant chain and the lower oxidation state metal (k_d) can be seen in Figure 2.20. Because of both initiation and deactivation are fast the molecular weight can controlled, allowing for all the chains to begin growing at approximately the same time while maintaining a low concentration of active species. However, the proportion of chains terminated compared to the number of propagating chains is small,termination step can not be entirely avoided [36].To catalyze this process several metal/ligand systems have been used and variety of monomers including styrene, methacrylates, and acrylonitrile have been succesfully polymerized [37-39].

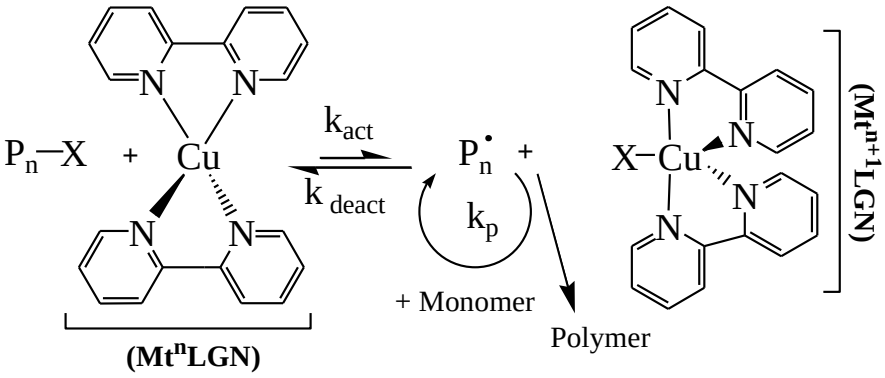


Figure 2.6: Mechanism of ATRP.

Internally first order in monomer is the rate of ATRP, externally first order with respect to initiator and activator, Cu(I),and negative first order with respect to deactivator, XCu(II).The actual kinetics based on many factors such as; the solubility of activator and deactivator, their possible interactions, and variation of their structures and reactivities with concentrations and composition of the reaction medium. The dynamics of exchangeis one of the most important parameters in ATRP, especially the relative rate of deactivation. Provided that the deactivation process is slow than propagation, then a classic redox initiation process operates leading to conventional, and not controlled, radical polymerization. Polydispersities (PDI) in ATRP will be lower with conversion, with the rate constant of deactivation, k_d, and also with the concentration of deactivator, [XCu(II)]. However, they increase with the propagation rate constant, k_p, and the concentration of initiator, $[RX]_o$. This means that more uniform polymers with higher conversion are obtained, when the concentration of deactivator in solution is high and the concentration of initiator is low. Moreover, more uniform polymers are formed when deactivator is very reactive and monomer propagates slowly (styrene rather than acrylate) [40].

2.6.2 Kinetics of ATRP

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivator (CuX_2 / Ligand). The rate equation of ATRP is formulated in discussed conditions and given in Figure 2.7.

$$R_p = k_{app}[M] = k_p[P\cdot][M] = k_p K_{eq}[I]_0 \frac{[Cu(I)]}{[Cu(II)X]}[M]$$

Figure 2.7: The rate equation of ATRP.

Results from kinetic studies of ATRP for styrene [41], methyl acrylate (MA) [42], and methyl methacrylate (MMA) [43, 44] under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator, and Cu(I) complex concentrations.

If the deactivation does not occur, if it is too slow ($k_p >> k_d$), there will be no difference between ATRP and the classical redox reactions and the termination and transfer reactions may be observed. To gain better control over the polymerization, addition of one or a few monomers to the growing chain in each activation step is desirable. Molecular weight distribution for ATRP is given in Figure 2.8.

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_d[RX]_0}{k_p[XCu^{II}]}\right)\left(\frac{2}{p} - 1\right)$$

p= poymerization yield
$[RX_0]$=concentration of the functional polymer chain
$[XCu^{II}]$=concentration of the deactivators
k_d=rate of deactivation
k_p=rate of propagation

Figure 2.8: Molecular weight distribution for ATRP.

When a hundred percent of conversion is reached, in other words p=1, it can be concluded that;

a) For the smaller polymer chains, higher polydispersites are expected to be obtained because the smaller chains include little activation-deactivation steps resulting in little control of the polymerization.

b) For the higher ratios of k_p / k_d, higher polydispersities (molecular weight distributions) are usually obtained.

c) Resulting molecular weight distribution decreases as the concentration of the deactivators increases.

The ATRP equilibrium can be theoretically broken down into 4 separate reversible reactions (Figure 2.9). It is important to note that while analysis of the ATRP equilibrium as dissected into these four elementary steps can generate useful trends, the physical relevance to how the reaction proceeds is less meaningful. The four reversible reactions are: oxidation of the metal complex (electron transfer, K_{ET}), alkyl halide bond homolysis (K_{BH}), reduction of a halogen to a halide ion (electron affinity, K_{EA}), and association of the halide ion to metal complex (halidophilicity, K_X) [45]. The product of these four elementary rate constants gives rise to the overall ATRP equilibrium (K_{ATRP}).

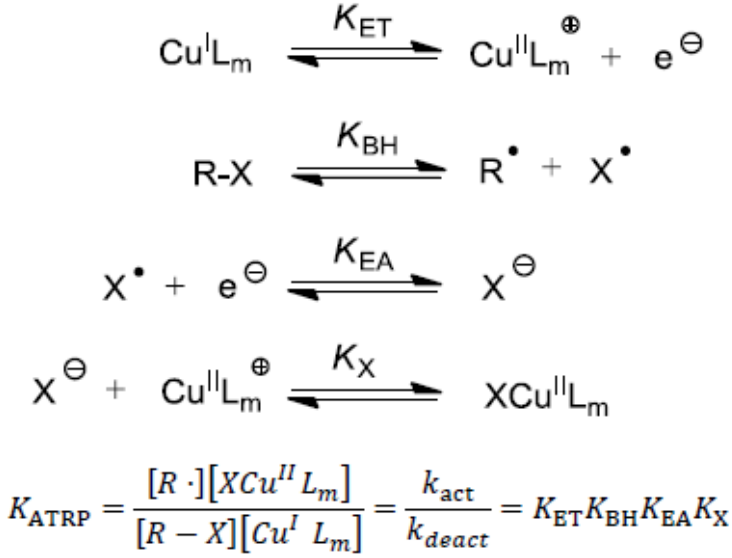


Figure 2.9: Breakdown of ATRP equilibrium.

2.6.3 Components of ATRP

2.6.3.1 Monomers

Monomers: In ATRP, a variety of monomers, such as styrenes, (meth)-acrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyridine and diens can be used to obtained well-defined polymers. However, even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium

constant for its active and dormant species [46]. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant ($K_{eq}=k_{act}/k_{deact}$) determines the polymerization rate.

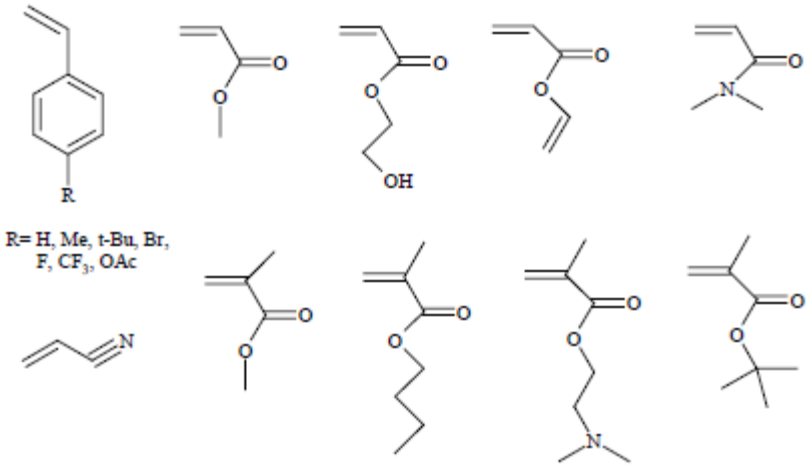
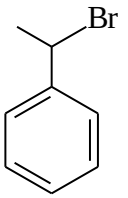
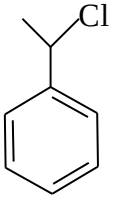
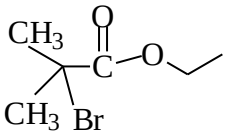
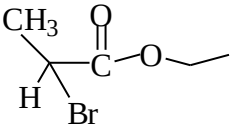
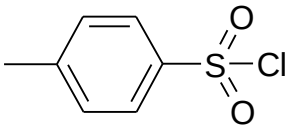


Figure 2.10: Examples of monomers that can be used in ATRP.

2.6.3.2 Initiators

To determining the number of growing polymer chain initiator is used. R-X are typically used as the initiator in ATRP and the rate of the polymerization is first order with respect to the concentration of R-X [47]. Initiation should be fast in comparison with propagation and the probability of the side reactions should be minimized are two important parameters for a successful ATRP initiating system. In ATRP, alkylhalides (RX) are typically used as initiator and the rate of polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex. When X is either bromine or chlorine, the molecular weight control is the best. Flourine is not used because the C-F bond is too strong to undergo homolytic cleavage [48].

Table 2.1: The most frequently used initiator types in ATRP systems.

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo isobutyrate	Methylmethacrylate
 Ethyl-2-bromo propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methylmethacrylate

2.6.3.3 ligands

Solubilizing the transition metal salt in the organic media and to adjust the redox potential of the metal center for the atom transfer are the main roles of ligand in ATRP that allows homogeneous redeox process during the polymerization [49,50] .

There are five guidelines for an efficient ATRP catalyst. First fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkylhalide and the transition metal is strongly shifted

toward the dormant species side. This equilibrium position will render most of the growing polymer chainsdormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution. Fourth relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate.Fifth, there should be no side reactions such as β-H abstraction or reduction/oxidation of the radicals.

The derivatives of 2,2-bipyridine and nitrogen based ligands such as *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA), tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine(HMTETA), tris[2-(dimethylamino) ethyl]amine (Me-TREN) are the most widely used ligands for ATRP systems, alkylpyridylmethanimines are also used.

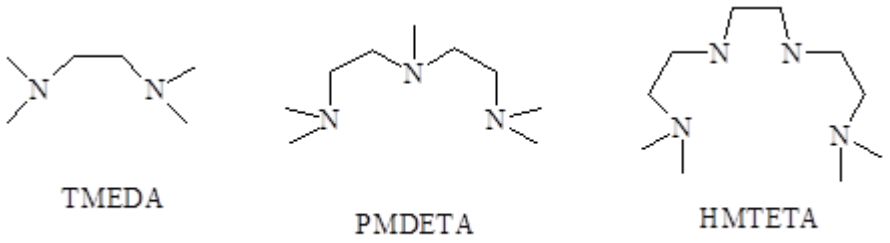


Figure 2.11: Nitrogen based ligands.

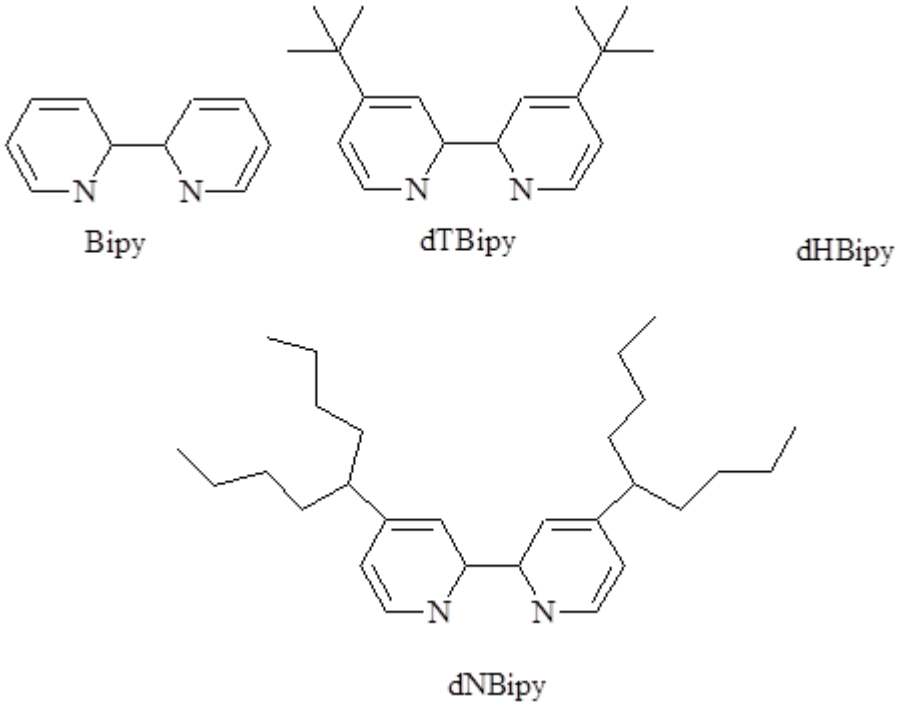


Figure 2.12: Derivatives of 2,2-bipyridine ligand.

2.6.3.4 Solvents

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g. emulsion,suspension). Various solvents such as aliphatic and aromatic have been used for different monomer types in ATRP reaction. Only halogenated solvents can not used in ATRP. Three major factors can affect the choice of solvent first one is; solubility of monomer, polymer and the catalyst, second one is minimal chain transfer and side reaction involving solvent, third one is acceleration and better control of polymerization. Benzene, tolüene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many other solvents are used for different monomer types [51].

2.6.3.5 Catalsyts

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. Prerequisites for an efficient transition metal catalyst seperated into four. First, the metal center must have at least

two readily accessible oxidation states separated by one electron. Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)- halogen. Fourth, the ligand should complex the metal relatively strongly. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. A variety of transition-metal complexes have been studied as ATRP catalysts such as ruthenium, iron, rhodium, copper, nickel, rhenium, palladium, and molybdenum [31]. The most extensively studied catalyst is copper halide. The Cu(I) based catalyst was first reported by Wang and Percec for the polymerization of styrene [52]. Cu(I) systems have been subsequently applied for a wide range of monomers ever since.

2.6.4 Limitations of ATRP and future perspective

Most of functional groups which in the monomer are not tolerated in ATRP these are carboxylic acid and certain ionic groups, which react with the catalyst, thereby impeding the establishment of the equilibrium.Carboxylic acid groups can, however, be introduced by polymerization of the carboxylic acid salt instead. This was first realized by the group of Armes, who polymerized methacrylic acid in aqueous media at pH∼9 using a poly(ethylene oxide) macroinitiator. Some monomers like vinyl acetate and halogenated alkenes can not be polymerized by atom transfer radical polymerization, because of insufficient stabilization of the formed radical.

ATRP has been used industrially for several years with commercial products being manufactured in the US, Japan, and Europe [53]. Removal of the catalyst is the main concern in using atom transfer radical polymerization for synthesis, industrial or otherwise process.The metal catalyst-ligand complex is undesired in the product, as the transition metal induces aging in the polymer, but also for aesthetic (coloration) and toxicological reasons removal is important. Catalyst removal is both difficult and costly, but several methods are presently in use. One procedure is to immobilize the catalyst by having it attached to solid supports during reaction, but this can give loss of control, perhaps due to reduced mobility. Other purification methods include

passing the raw product through an alumina column, precipitation of polymer and use of an absorbant [54].

Future perspective about the catalyst remove method from the polymers is Lower ppm Cu Process [55]. This problem has been partially resolved by using low ppm Cu processes, but further exploration of most efficient and economic ways to remove and reclaim residual Cu is needed; they may include special absorbents, smart systems responsive to external stimuli, electrodeposition, and other as yet unexplored techniques.

3. EXPERIMENTAL PART

3.1 Materials

2-Bromopropionly bromide (97%, Sigma Aldrich) is used as received. Density is 2.06g/ml.

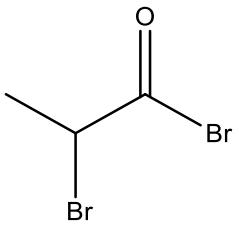


Figure 3.1: 2-Bromopropionyl bromide.

Triethylamine (TEA, 99%, Acros) is used as received. Density is 0.7255 g/ml.

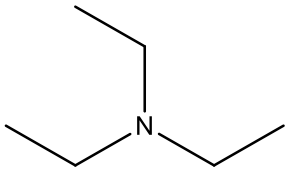


Figure 3.2: TEA.

4-Dimethylaminopyridine (DMAP, 98%, Fluka) is used as received. M_w is 112.17 g/mol.

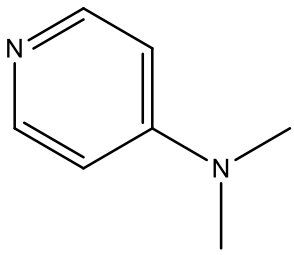


Figure 3.3: DMAP.

Chloroform($CHCl_3$, 99%, Merck) is used as received. Density is 1.49g/ml.

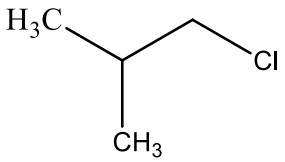


Figure 3.4: $CHCl_3$.

Dimethylformamide (DMF, ≥|99.5%, Merck) is used as received. Density is 0.948 g/ml.

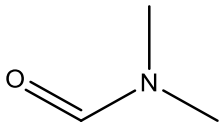


Figure 3.5: DMF.

Methyl methacrylate (MMA, 98%, Fluka) was passed through an alumina column with basic alumina before use to remove the inhibitor.

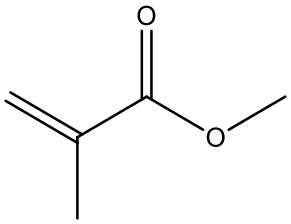


Figure 3.6: MMA.

Anisole (≥99%, Acros) is used as received. Density is 0.995 g/ml.

Copper(I)bromide (98%, Sigma Aldrich) is used as received.

***N,N,N',N',N''*-pentamethyldiethylentriamine (PMDETA, 97%, Aldrich)**

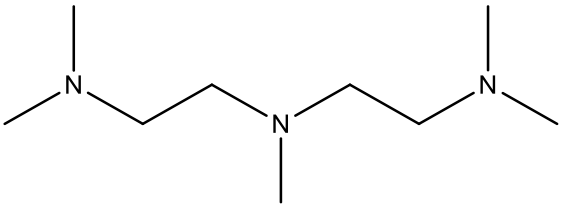


Figure 3.7: PMDETA.

Tetrahydrofuran (THF, 99.8 %, J. T. Baker)

ethyl-2-bromoisobutyrate (2EIBr, 99.8%, Alfa Aesar)

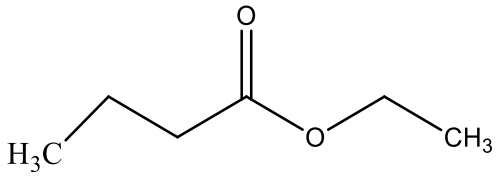


Figure 3.8: 2EIBr.

Methly alcohol (≥99%, Sigma) is used as received.

Dimethylsulfoxide-D6 (DMSO, 99.8%, Merck)

Chloroform-D1 ($CdCl_3$, 99.8%, Merck)

3.2 Equipments

3.2.1 Nuclear magnetic resonance (NMR)

^{1}H-NMR spectra was obtained at suitable temperature on a Agilent VNMRS 500 MHz spectrometer using deuterated chloroform ($CDCl_3$-d_1) and Deuterated dimethyl sulfoxide (DMSO-d_6) were used as solvent.

3.2.2 Gel permeation chromatography (GPC)

Molecular weights were analyzed using gel permeation chromatography (GPC). GPC analysis were carried out with a set up consisting of the Agilent pump and refractive index detector and three Agilent Zorbax Columns (1000S, 300S, and 60S). THF was used as the eluent at a flow rate of 0.5 mL/min at 30 ^{o}C. M_ws were calculated with the aid of pMMA standards.

3.2.3 Fourier transform infrared spectroscopy (FT-IR)

Analyses were performed with Thermo Scientific Nicolet IS FT-IR Spectrometer. Resolution mode is 4 cm^{-1}. Sixteen scans were averaged for each sample in the range 4000-400 cm^{-1}.

3.2.4 Differential scanning calorimetry (DSC)

Analyses were performed with TA DSC Q10 instrument in a flowing nitrogen atmosphere. First cycle from 10 to 180 ^{o}C at a rate of 10 $^{o}C/min^{-1}$, second cyle from 180 to 10 ^{o}C , third cycle from 180 to 350 ^{o}C. The weights of samples are between 2-5 mg.

3.2.5 Thermogravimetric analyser (TGA)

Analyses were permormed with TA Q50 instrument under the nitrogen atmosphere at a heating rate of 20°C/min rising rom room temperature to 950°C. The weights of samples are between 5-15 mg.

3.3 Synthesis

3.3.1 Synthesis of CBM and CBM-Br

To a solution of *o*-carborane (1 eq) and formaldehyde (1 eq) in THF (10 mL) was added tetrabutylammonium fluoride (TBAF) (1.0 M in THF, 3 eq) under Ar atmosphere, and the mixture was stirred at room temperature for 30 min. The reaction was quenched by saturated aqueous NH_4Cl, and the mixture was extracted with ether, washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and then concentrated. Purification by silica gel column chromatography chloroform.

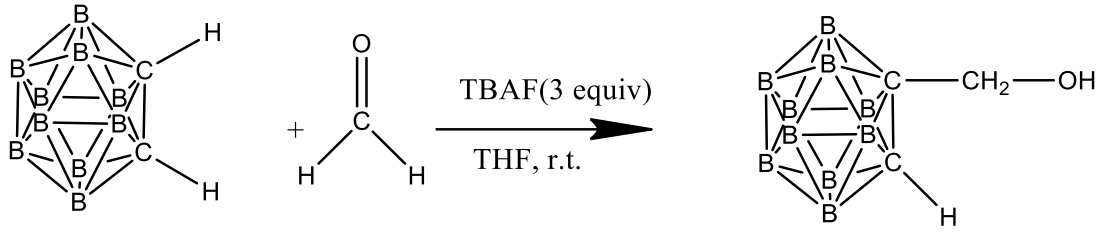


Figure 3.9: Synthesis of carboranemonool.

Carboranemonool was synthesized according to procedure [56-58]. (0.4 g, 2.45 mmol), TEA (3.721mmol, 0,51mL), DMAP (0.245 mmol, 0.029 g) were added to the three-necked flask charged with chloroform ($CHCl_3$, 7 mL) and cooled to 0°C under a nitrogen atmosphere. 2-bromopropionyl bromide (3.67 mmol, 0.38 mL) was added dropwise to the solution, the mixture was stirred for 1 hour at 0°C and then 3 hours at room temperature. The reaction mixture was washed with water (3 x 20 mL) and deionized water and 5% Na2CO3 solution. Then dried overnight with MgSO4. After filtration and evaporation of $CHCl_3$ a sticky light brown, very viscose product was obtained. It was dissolved in ethylacetate and precipitated into the hexane. It was dried under vacuum. Yield was 55.4%.

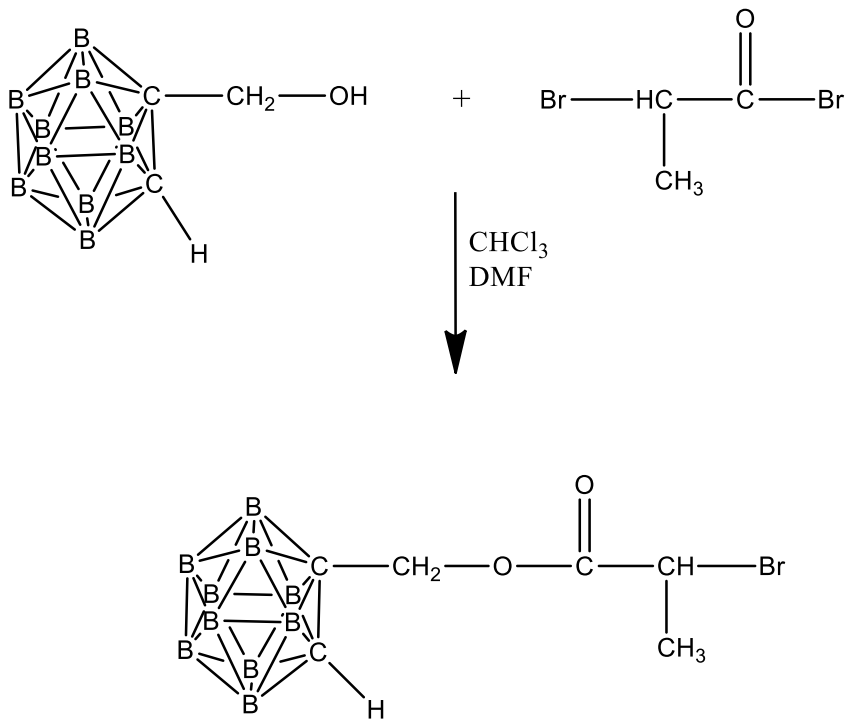


Figure 3.10: Synthesis of monofunctional initiator CBM-Br for ATRP.

3.3.2 Synthesis of CBD and CBD-Br

A 1.53 M solution of n-BuLi in n-hexane (10.43 mL, 5.96 mmol) was added dropwise to a solution of o-$C_2B_{10}H_{12}$ (1 g, 6.94 mmol) in a dry toluene/Et_2O mixture (2:1, 30 mL) with stirring at 0°C. The mixture was allowed to warm to room temperature and stirred for 90 min. The solution was then cooled to 0°C, and a solution of oxetane (1.03 ml, 15.96 mmol) in toluene/ Et_2O (2:1, 10 mL) was added with stirring. The reaction mixture was stirred at room temperature overnight and then quenched with 50 mL of water. The organic layer was separated, and the aqueous layer was extracted with Et_2O (30 mL x 2). The combined organic portions were dried over anhydrous Na_2SO_4 . Removal of the solvents gave a white solid that was washed with n-hexane (10 mL x 2) and dried under vacuum to afford as a white powder (1.5 g, 83%).

Recrystallization from dichloromethane yielded colorless crystals.

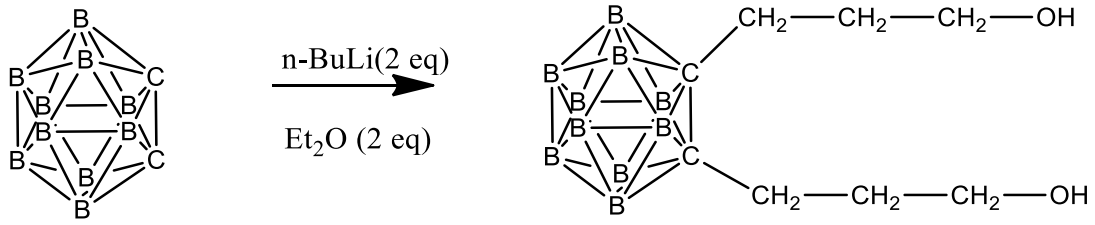


Figure 3.11: Synthesis of carboranediol.

Carboranediol was synthesized according to procedure [56-58]. (0.4 g, 1.536 mmol), TEA (2.304 mmol, 0.32 mL.), DMAP (0.230 mmol, 0.028 g) were added to the three-necked flask charged with chloroform ($CHCl_3$, 7 mL) and cooled to 0°C under a nitrogen atmosphere. 2-bromopropionyl bromide (3.84 mmol, 0.4mL) was added dropwise to the solution, the mixture was stirred for 1 hour at 0°C and then 3 hours at room temperature. The reaction mixture was washed with water (3 x 20 mL) and deionized water and 5% Na2CO3 solution. Then dried overnight with MgSO4. After filtration and evaporation of $CHCl_3$ a sticky light brown, very viscose product was obtained. It was dissolved in ethylacetate and precipitated into the hexane. It was dried under vacuum. Yield was 54.8%.

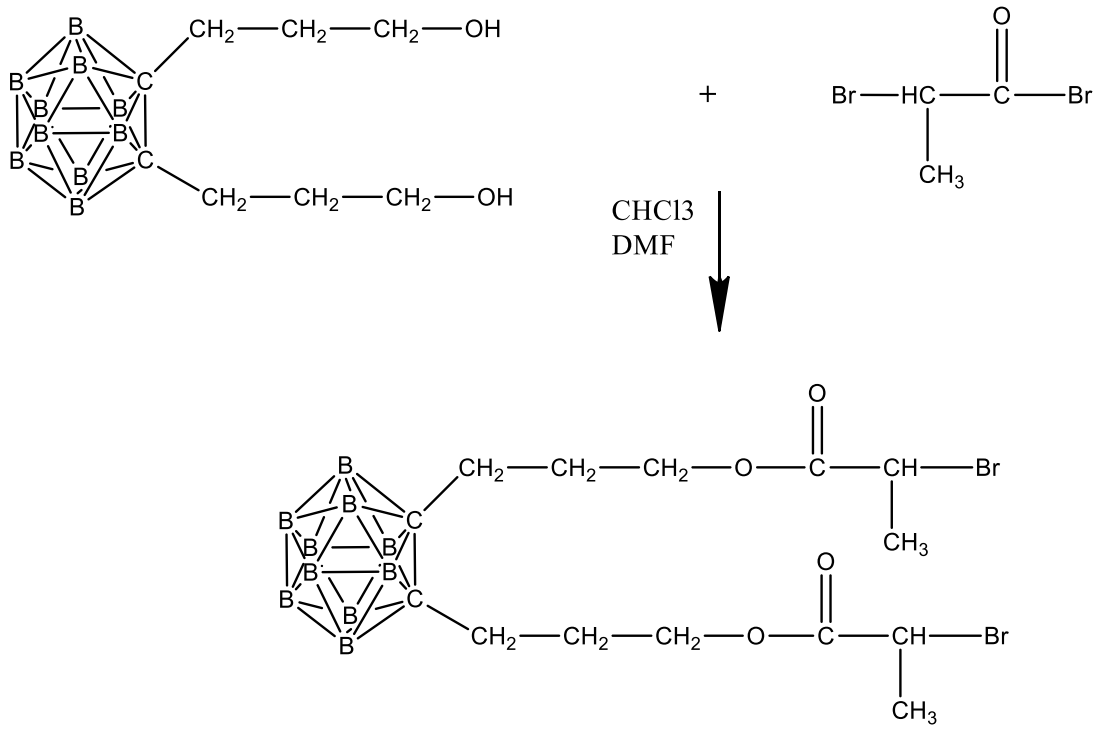


Figure 3.12: Synthesis of bifunctional initiator CBD-Br for ATRP.

3.3.3 Polymerization of MMA with initiator CBM-Br

To a schlenk tube equipped with magnetic stirrer, vacuum and dry nitrogen was applied three times, then 1 mL (9.288 mmol) MMA and anisole 1 mL (9.200 mmol) were added as solvent. 0.0266 g (0.185 mmol) copper(I) bromide, 64 µL (0.306mmol) ligand (PMDETA), and initiator 0.0138 g (0.093mmol) CBM-Br were added under nitrogen. The reaction solution was bubbled by nitrogen to remove dissolved gases and then the tube was immersed in an oil bath and held by thermostat at 90ºC. The polymerization was performed for 15, 45, 60, 90 and 180 min then terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF. The THF solution was passed through a short alumina column to remove copper complex and then concentrated by evaporation. The polymer was precipitated into excess methanol and filtered. The filtrate was dried under vacuum. The conversion was determined gravimetrically. ATRP conditions and results are given in Table 3.1

Table 3.1: Polymerization characteristics of polymethylmethacrylates with CBM-Br.

Run	Time (min)	Conv. (%)[b]	$M_{n,th}$[c]	$M_{n,exp}$[d]	M_w/M_n[d]
CBM-pMMA1	15	4	800	4400	1.6
CBM-pMMA2	45	23	4600	12500	1.5
CBM-pMMA3	60	26	5200	17000	1.5
CBM-pMMA4	90	27	5400	23700	1.4
CBM-pMMA5	180	29	5800	45000	1.3
pMMA (control)	120	29	5800	10550	1.1

[a] $[Monomer]_o$: $[I]_o$: $[CuBr]_o$: $[PMDETA]_o$ = 200 : 1 : 4 : 8 in anisole at 90°C for pMMA.
[b] Determined gravimetrically.
[c] Calculated by *Mn*, th = ($[M_o]$ / $[I_o]$) x (conversion %) x $Mn_{monomer}$
[d] Determined by means of GPC calibrated with pMMA standards.

3.3.4 Polymerization of MMA with initiator CBD-Br

To a schlenk tube equipped with magnetic stirrer, vacuum and dry nitrogen was applied three times, then 1 mL (9.288 mmol) MMA and anisole 1 mL (9.200 mmol) were added as solvent. 0.0266 g (0.185mmol) copper(I) bromide, 77µL (0.370 mmol) ligand (PMDETA), and initiator 0.0246 g (0.046 mmol) CBD-Br were added under nitrogen. The reaction solution was bubbled by nitrogen to remove dissolved gases and then the tube was immersed in an oil bath and held by thermostat at 90 ^oC. The polymerization was performed for 5, 7, 8, and 15 h then terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF. The THF solution was passed through a short alumina column to remove copper complex and then concentrated by evaporation. The polymer was precipitated into excess methanol and filtered. The filtrate was dried under vacuum. The conversion was determined gravimetrically. ATRP conditions and results are given in Table 3.2

Table 3.2: Polymerization characteristics of polymethylmethacrylates with CBD-Br.

Run	Time (h)	Conv. (%)[b]	$M_{n,th}$[c]	$M_{n,exp}$[d]	M_w/M_n[d]
CBD-pMMA1	5	17	3400	6500	1.6
CBD-pMMA2	7	40	8000	16700	1.5
CBD-pMMA3	8	43	8600	16500	1.5
CBD-pMMA4	15	48	9600	27000	1.4
pMMA (control)	2	29	5800	10550	1.1

[a] $[Monomer]_o$: $[I]_o$: $[CuBr]_o$: $[PMDETA]_o$ = 200 : 1 : 4 : 8 in anisole at 90°C for pMMA.
[b] Determined gravimetrically.
[c] Calculated by *Mn*, th = ($[M_o]$ / $[I_o]$) x (conversion %) x $Mn_{monomer}$
[d] Determined by means of GPC calibrated with pMMA standards.

3.3.5 Polymerization of MMA with initiator ethyl-2-bromoisobutyrate

To a schlenk tube equipped with magnetic stirrer, vacuum and dry nitrogen was applied three times, then 1 mL (9.288 mmol) MMA and anisole 1 mL (9.200 mmol) were added as solvent. 0.0266 g copper(I) bromide, 77µL ligand (PMDETA), and initiator 6.85µL 2EIBr was added under nitrogen. The reaction solution was bubbled by nitrogen to remove dissolved gases and then the tube was immersed in an oil bath and held by thermostat at 90 ^oC. The polymerization was performed 2 h then terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF. The THF solution was passed through a short alumina column to remove copper complex and then concentrated by evaporation. The polymer was precipitated into excess methanol and filtered. The filtrate was dried under vacuum. The 29% conversion was determined gravimetrically. ATRP conditions and results of pMMA(control) are given in Table 3.1 and Table 3.2 .

4. RESULTS AND DISCUSSION

In this thesis, CBM and CBD were functionalized to obtain initiator which was used for polymerization of methyl methacrylate. For this reason CBM and CBD were brominated to make reactive bromine groups. CBM-Br and CBD-Br were used for polymerization of methyl methacrylate. For characterization FT-IR, ^{1}H-NMR, ^{11}B-NMR GPC, DSC, TGA, techniques were used.

4.1 Synthesis of CBM-Br and CBD-Br

CBM-Br and CBD-Br were synthesized according to the procedure (Figure 3.10 and Figure 3.12) mentioned in section **3.3.1** and **3.3.2**. Reaction of CBM-OH or CBD-OH with 2-bromopropionyl bromide, in the presence of DMAP and TEA, in $CHCl_3$ at room temperature for three days gave CBM-Br and CBD-Br, respectively. The resulting product was checked by ^{1}H-NMR and FT-IR spectroscopy techniques.

The FT-IR spectra of CBM and CBM-Br are given in Figure 4.1. The differences between these two spectra are the dissappearance of the characteristic peak of hydroxyl group at 3516 cm^{-1} and the appearance of carboxyl group peak at 1745 cm^{-1} and 1737 cm^{-1} also C-Br band appearance at 725 cm^{-1}, C-O-C band arising at 1145-1190 cm^{-1}. The characteristic absorption peak around 2564 cm^{-1} is resulted from the stretching of B-H which comes from o-carborane.

The FT-IR spectra of CBD and CBD-Br are given in Figure 4.2. The differences between these two spectra are the dissappearance of the characteristic peakof hydroxyl group around 3266 cm^{-1} and the appearance of carboxyl group peak at 1736 cm^{-1} and C-Br band at 730 cm^{-1}. C-O-C band arising at 1145-1240 cm^{-1}. The characteristic absorption peak around 2576 cm^{-1} is come from the stretching of B-H which comes from *o*-carborane.

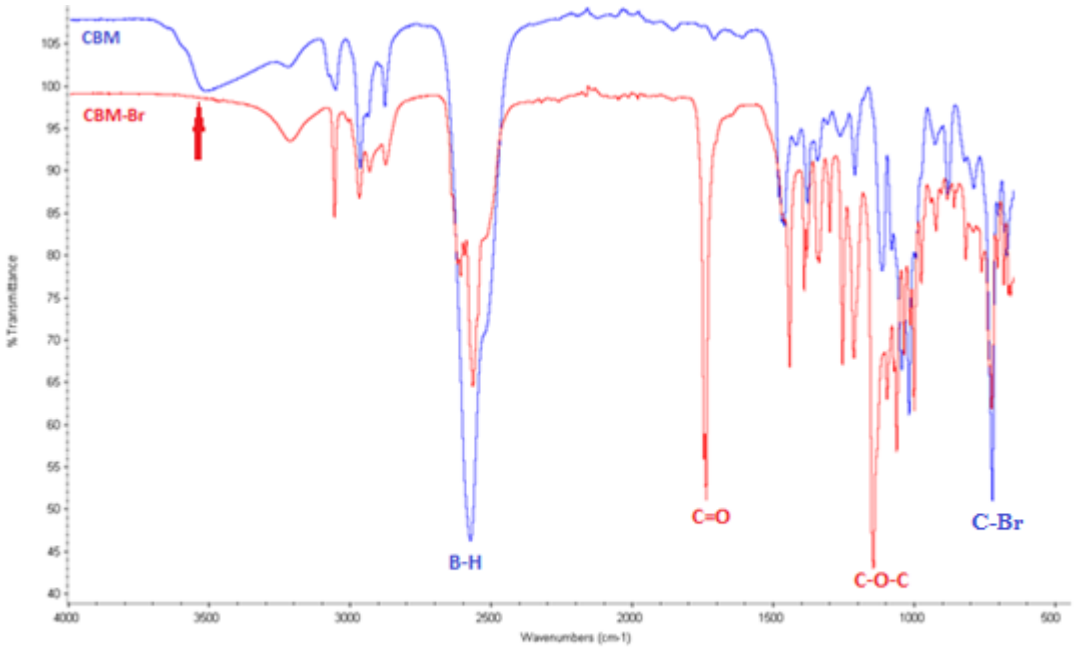


Figure 4.1: FT-IR spectrum of CBM and CBM-Br.

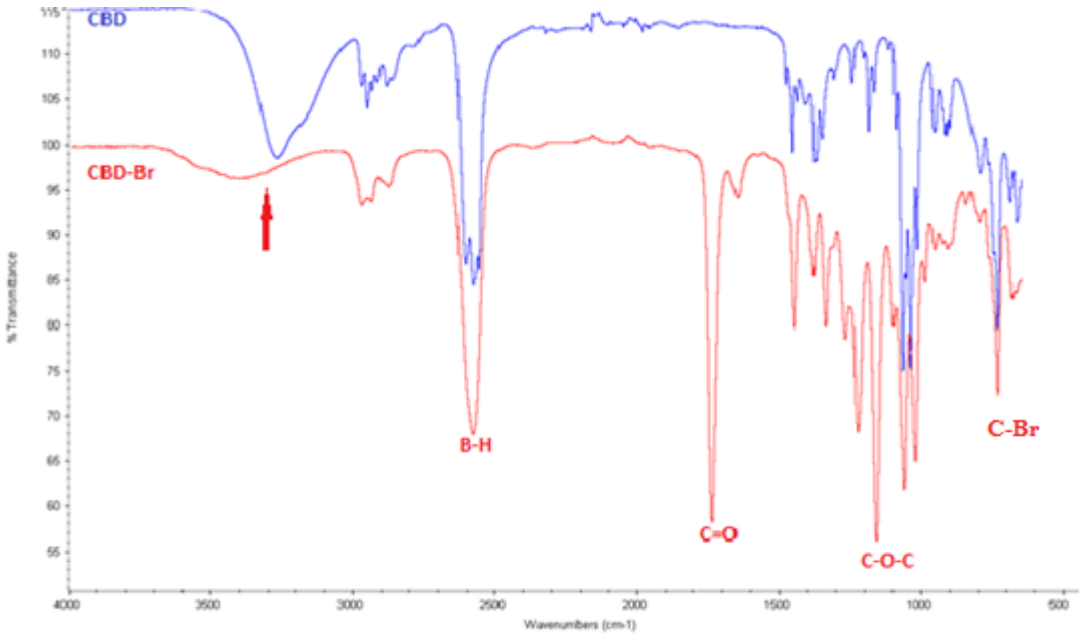


Figure 4.2: FT-IR spectrum of CBD and CBD-Br.

^{1}H-NMR spectrum of CBM and CBM-Br were taken in $CDCl_3$ (is seen at 7.26 ppm) as shown in Figure 4.3 Figure 4.4. The spectrum proves the expected structure of the initiator CBM-Br.

For the CBM spectrum; presence of $C_{carborane}$-H protons was observed at 3.20 ppm (s,H), -OH protons at 4.0 ppm (s, H), -OCH_2 protons was appeared at 4.10 ppm.

For the CBM-Br spectrum; presence of $C_{carborane}$-H protons appeared at 3.40 ppm (s,H), CBM-Br new peaks were seen at 1.80 ppm (d,3H) and 4.40 ppm(q,H) corresponded to –CH_3 and CH-Br respectively. -OCH_2 protons at 3.80 ppm (s,2H).

^{1}H-NMR spectrum of CBD and CBD-Br were taken in DMSO-d_6 (is seen at 2.5ppm and 3.30 ppm) as shown in Figure 4.5 and Figure 4.6. The spectrum proves the expected structure of the initiator CBD-Br.

For the CBD spectrum; presence of protons –CH_2 at 1.60 ppm (m,2H) and 2.30 ppm (t,2H), at 3.40 ppm (t,2H) corresponded to -OCH_2 protons. –OH protons are seen at 4.60 ppm (t,H).

For the CBD-Br spectrum; 1.60 ppm (m,2H) and 2.40 ppm (t,2H) are corresponded to –CH_2 protons, -OCH_2 protons appeared at 3.40 ppm (t,2H), CH-Br and –CH_3 protons at 4.20 ppm(q,H) and 1.70 ppm (d,3H).

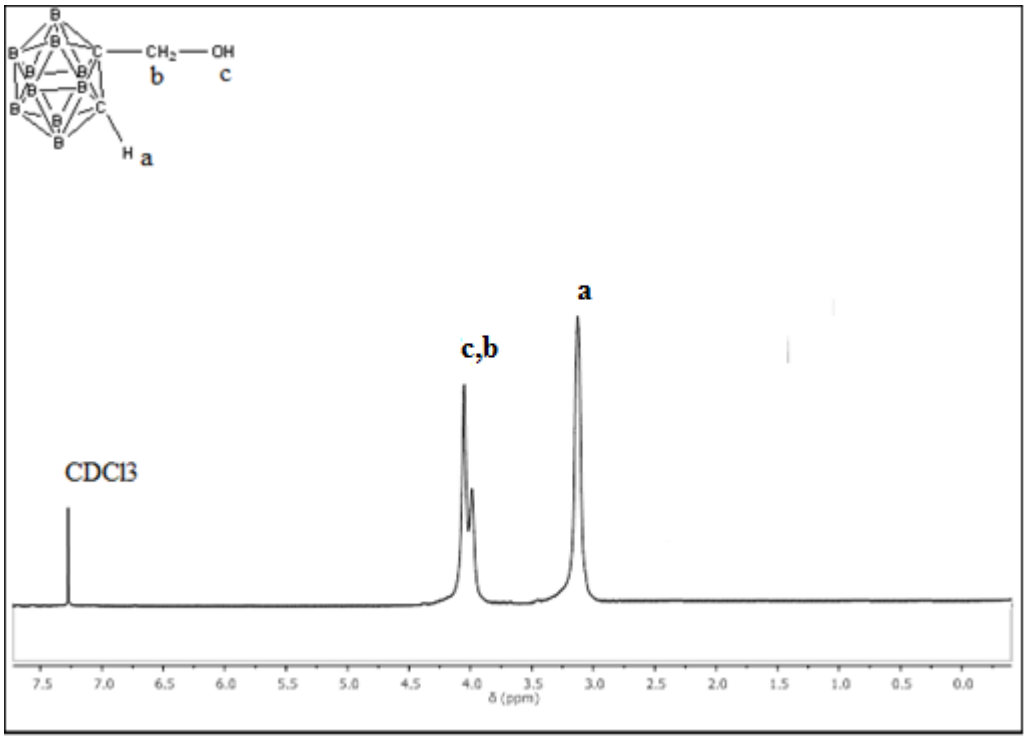


Figure 4.3: ^{1}H-NMR spectrum of CBM.

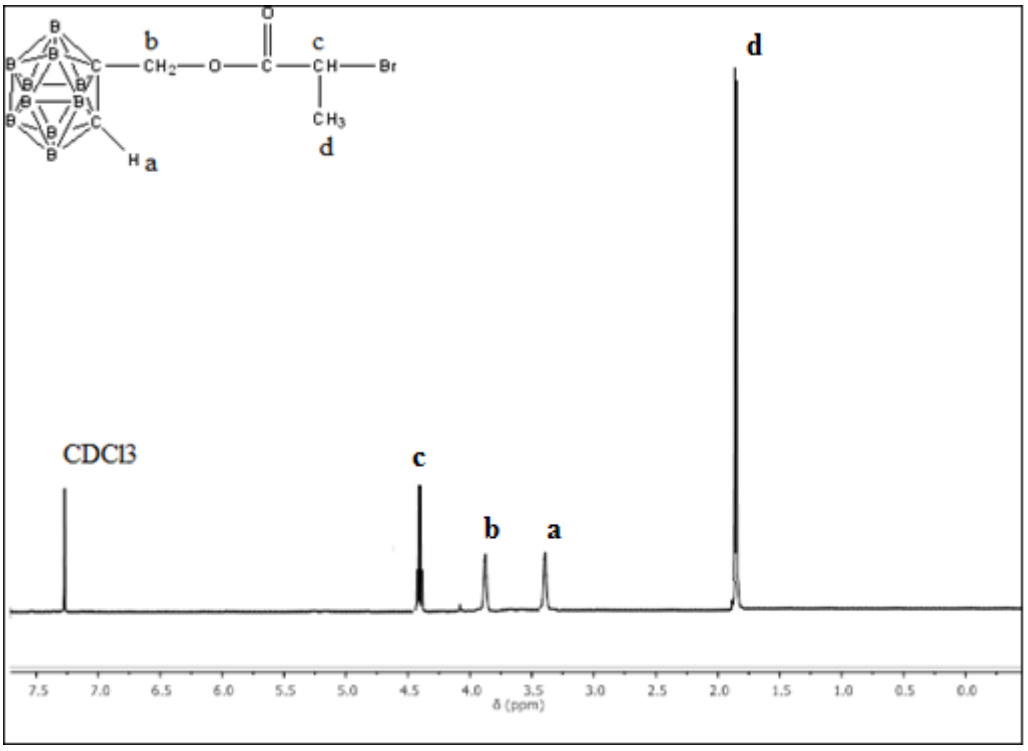


Figure 4.4: ^{1}H-NMR spectrum of CBM-Br.

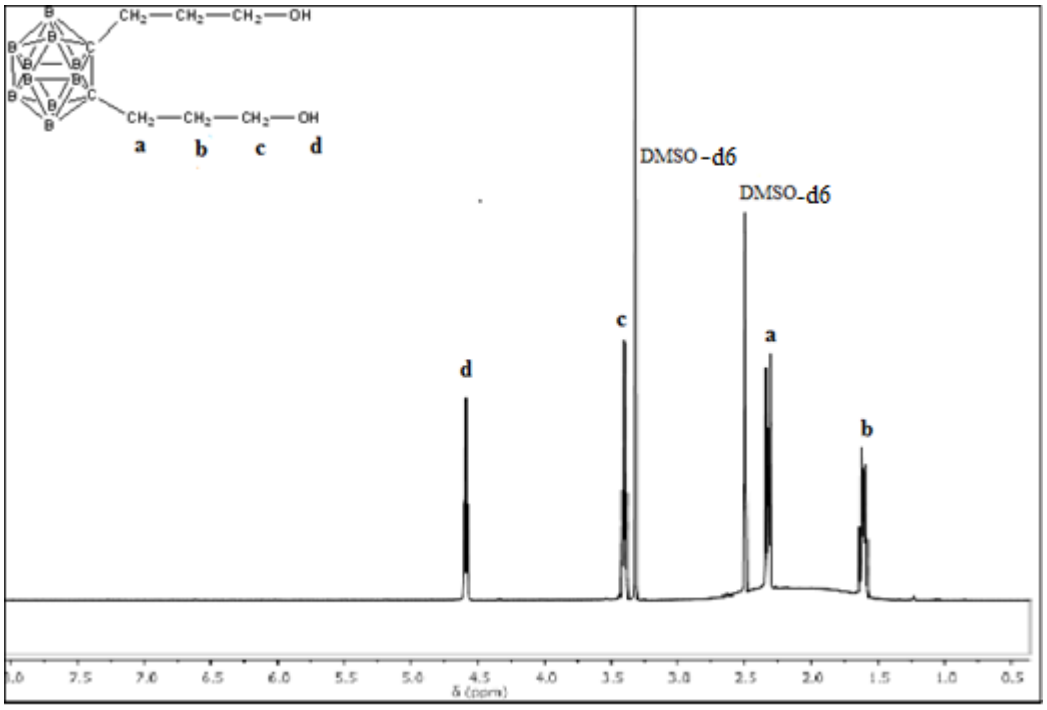


Figure 4.5: ^{1}H-NMR spectrum of CBD.

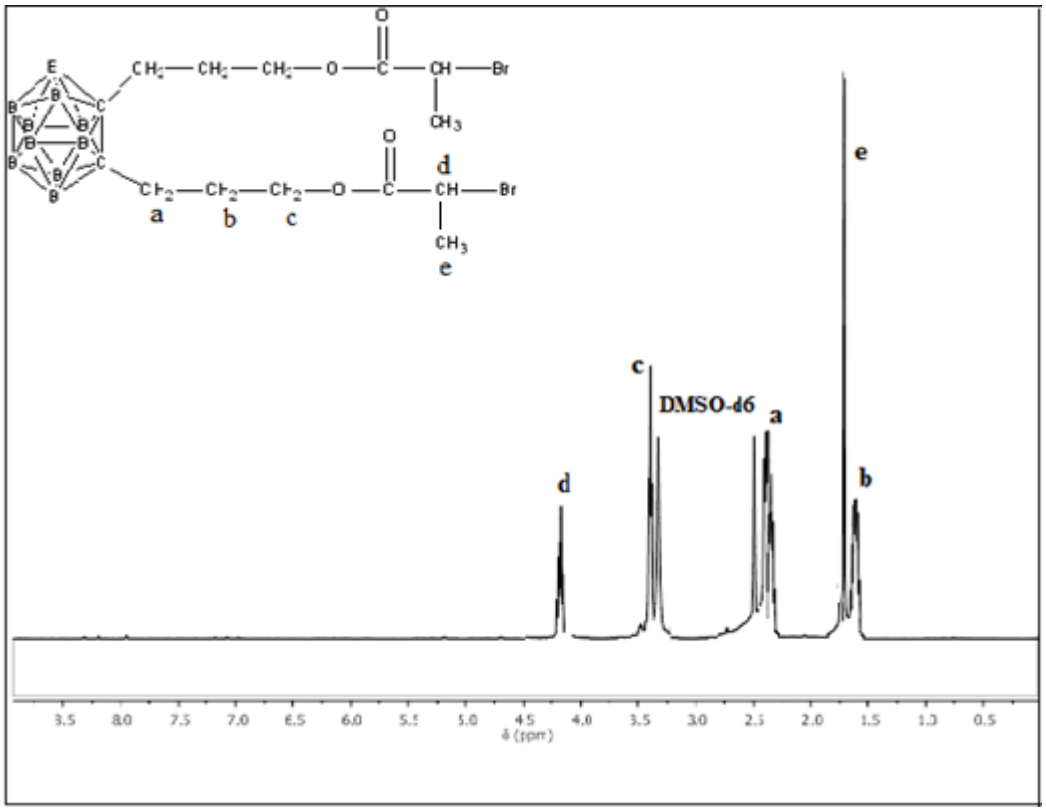


Figure 4.6: ^{1}H-NMR spectrum of CBD-Br.

4.2 ATRP of MMA With Monofunctional Initiator

MMA was polymerized by ATRP method in the presence of copper (I) bromide complexed with PMDETA ligand in Anisole solution. CBM-Br was used as the monofunctional initiator. Polymerization of MMA was carried out in Anisole solution at 90 ^{o}C using 1: 4: 8: 200 ratio of $[I]_o$ /[Cu+]/[PMDETA]/$[M]_o$. The results are summarized in Table 3.1. During the polymerization, the solutions became very viscous as the reaction time increased. The data demonstrate that the polymerization of MMA in Anisole has uncontrolled character resulting in rather broad molecular weight distribution (MWD) and higher experimental Mn values (GPC) than the calculated ones.The PDI values remain about 1.6 – 1.3. On the other hand, by increasing the time, the conversions of PMMA increase from 4 to 29%.

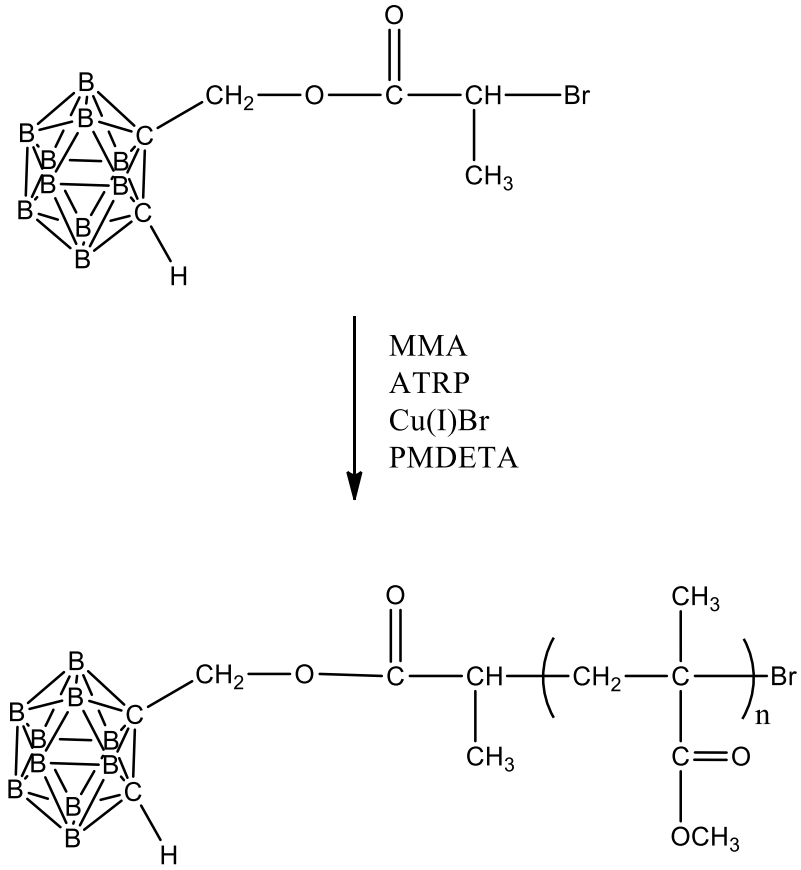


Figure 4.7: Synthesis of pMMA with monofunctional initiator CBM-Br.

Figure 4.6 shows, the semi-logarithmic kinetic plot of ln($[M]_o$/[M]) versus time, t, where $[M]_o$ is the initial concentration of the monomer, and [M] is the monomer

concentration at any time and also plots of Mn and polydispersity indexes (Mw / Mn) as a function of conversion. The linearity of the plot indicates that the concentration of growing radicals is constant. [M]/[I]/[Cu]/[PMDETA] = 200/1/4/8, [MMMA]o = 4.64 M for polymerization CBM-Br .

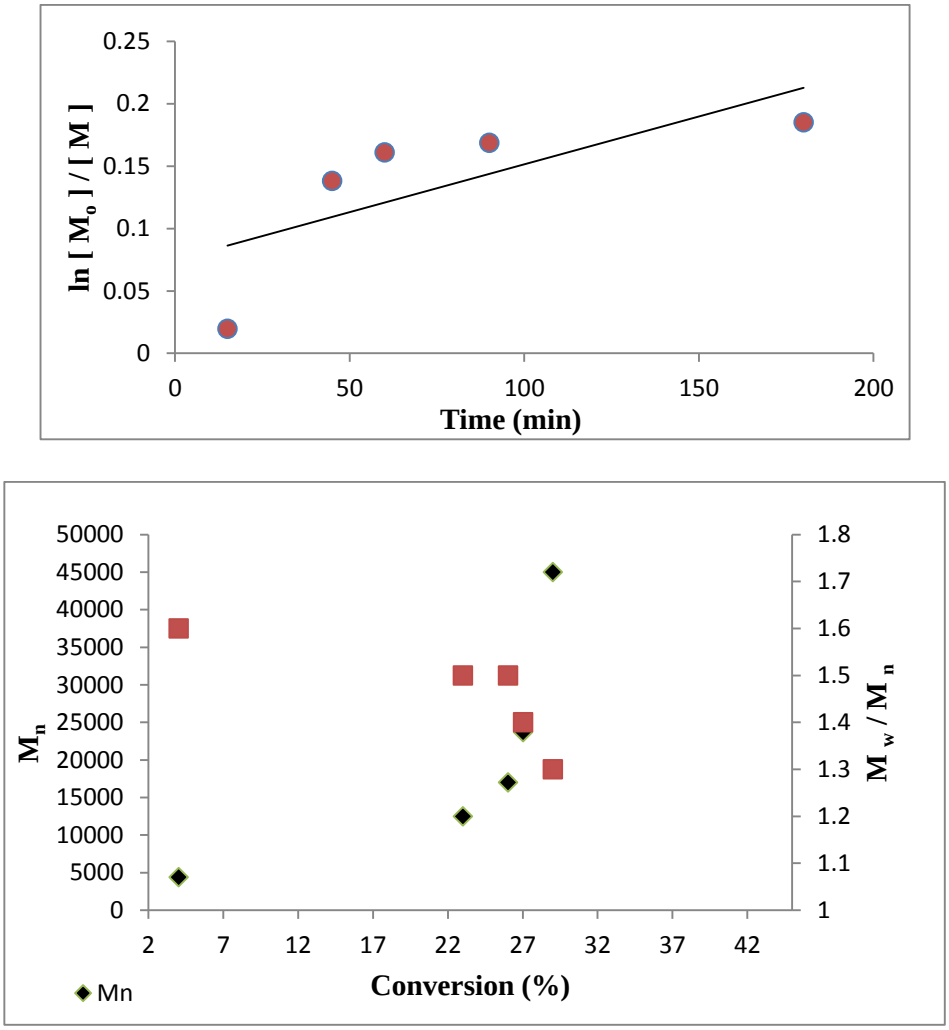


Figure 4.8: First order kinetic plots for polymerization of MMA using CBM-Br as initiator and CuBr as catalyst in anisole at 90 ^{o}C.

All CBM-pMMAs have the same FT-IR spectra which is shown in Figure 4.7. It can be seen that there was an absorption band from 1145 cm^{-1} to 1190 cm^{-1}, that could be connected to the C-O-C stretching vibration. α-methyl group vibrations appearance as two bands at 1387 cm^{-1} and 750 cm^{-1}. The band at 984 cm^{-1} was the characteristic absorption vibration of PMMA, together with the bands at 1062 cm^{-1} and 841 cm^{-1}. The band at 1725 cm^{-1} showed the presence of the acrylate carboxyl group. The band at 1438 cm^{-1} could be attributed to the bending vibration of the C-H bonds of the -

CH_3 group. The two bands at 2949 cm^{-1} and 2995 cm^{-1} could be assigned to the C-H bond stretching vibrations of the -CH_3 and -CH_2- groups. All of FT-IR spectrums prove that it could be the prepared polymer was indeed macromolecular PMMA [59]. The disappearance of C-Br signal proved that Br functions took part in initiating the PMMA chain growth.

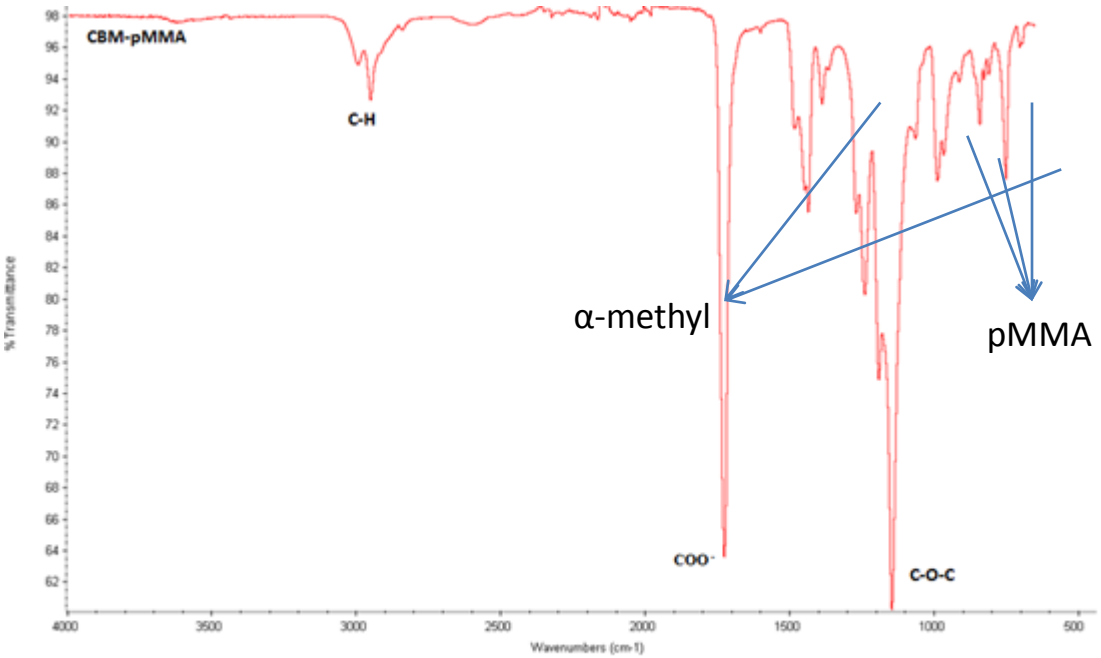


Figure 4.9: FT-IR spectrum of pMMA with monofunctional initiator.

^{1}H-NMR, in addition to the large absorption of the repeat units of pMMA, the characteristic signals were clearly visible Figure 4.10. The ^{1}H-NMR was taken in $CDCl_3$. The complete disappearance of initiator CBM-Br signals indicated that Br functions took part in initiating the pMMA chain growth.

The ^{1}H-NMR spectra of between 0.5 ppm and 2.0 ppm corresponded to the methylene protons of pMMAs, -OCH_2 and $C_{carborane}$ protons at 3.81 ppm (s,2H) and 3.79 ppm (s,H), -OCH_3 protons at 3.60 ppm (s,3H) sharp peak comes from pMMAs.

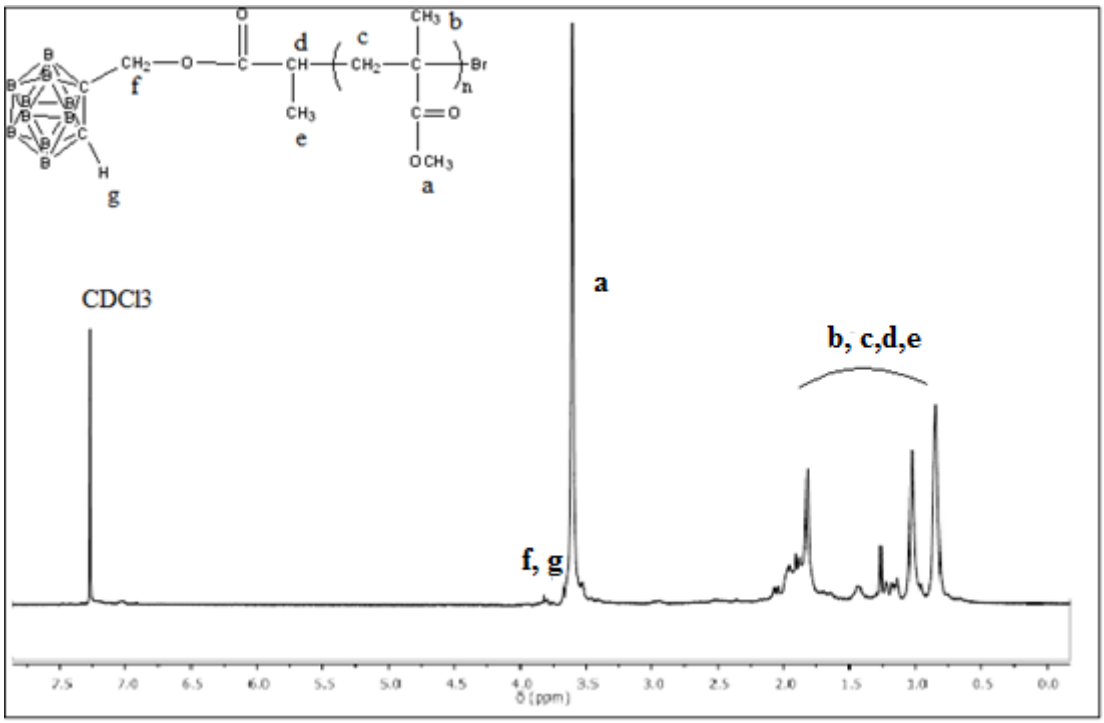


Figure 4.10: ^{1}H-NMR spectrum of CBM-pMMA.

For all monofunctional polymers have same ^{11}B-NMR peaks. In ^{11}B-NMR of CBM-Br as initiator , there is a sharp peak between 0 ppm and -40 ppm. After polymerization was ocuured, the peak remains 30 ppm and -20 ppm moreover it gets broader peaks for the CBM-pMMAs.

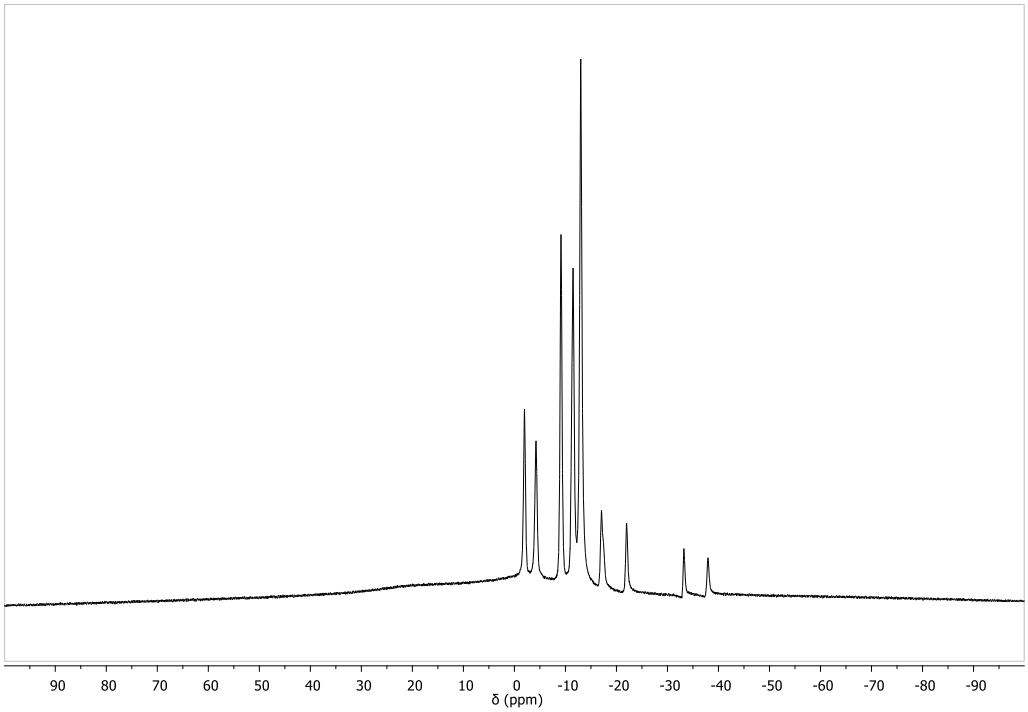


Figure 4.11: ^{11}B-NMR spectrum of CBM-Br.

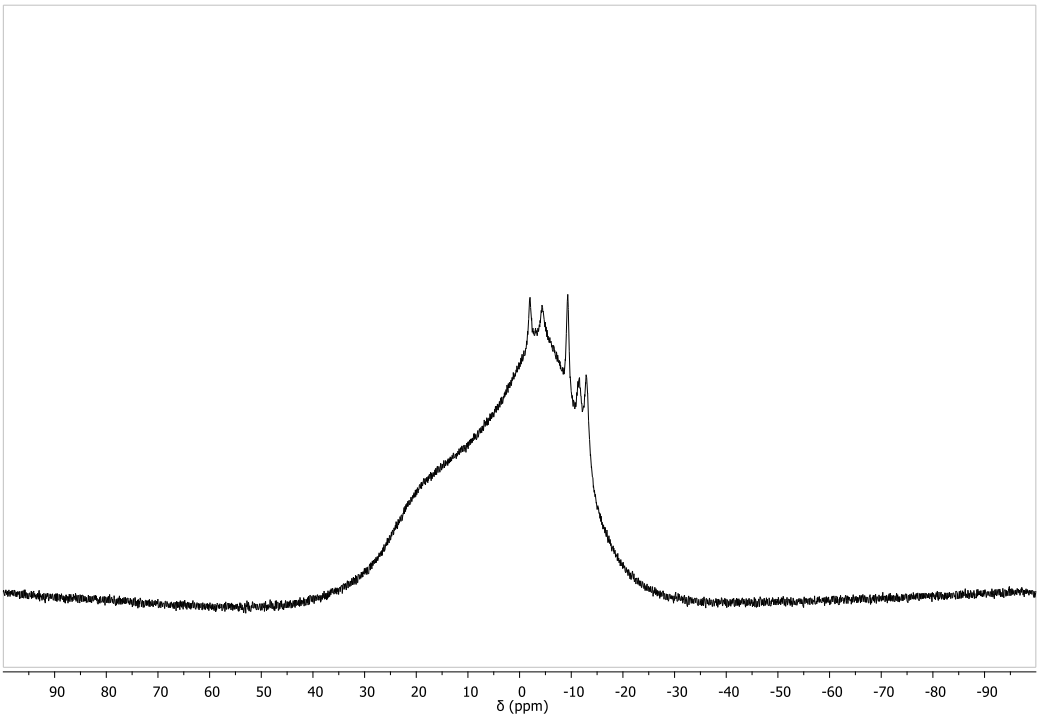


Figure 4.12: ^{11}B-NMR spectrum of CBM-pMMA.

4.3 ATRP of MMA With Bifunctional Initiator

MMA was polymerized by ATRP method in the presence of copper (I) bromide complexed with PMDETA ligand in Anisole solution. CBM-Br was used as the monofunctional initiator. Polymerization of MMA was carried out in Anisole

solution at 90 ºC using 1: 4: 8: 200 ratio of $[I]_o$ /[Cu+]/[PMDETA]/$[M]_o$. The results are summarized in Table 3.2. During the polymerization, the solutions became very viscous as the reaction time increased. The data demonstrate that the polymerization of MMA in Anisole has uncontrolled character resulting in rather broad molecular weight distribution (MWD) and higher experimental Mn values (GPC) than the calculated ones.The PDI values remain about 1.4 – 1.2. On the other hand, by increasing the time, the conversions of PMMA increase from 17 to 48%.

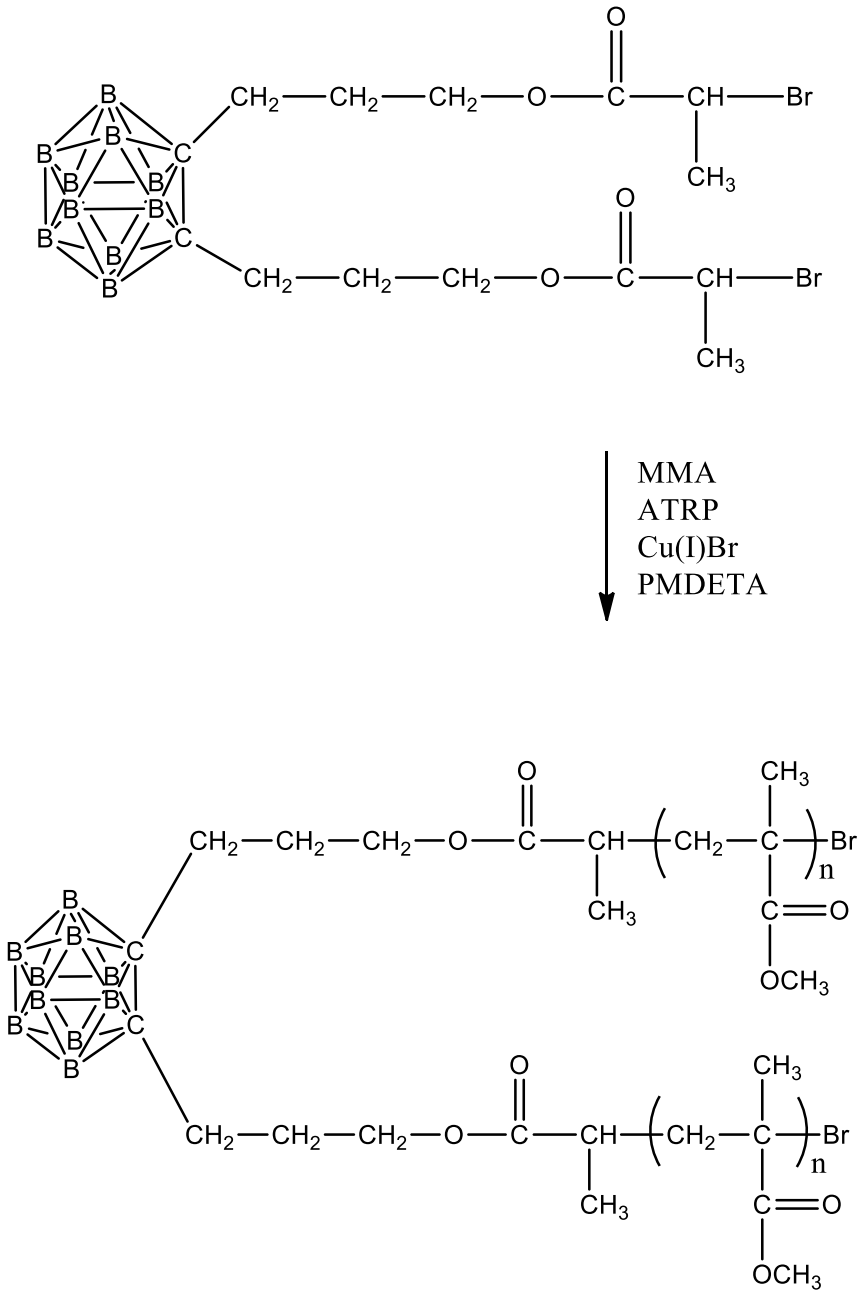
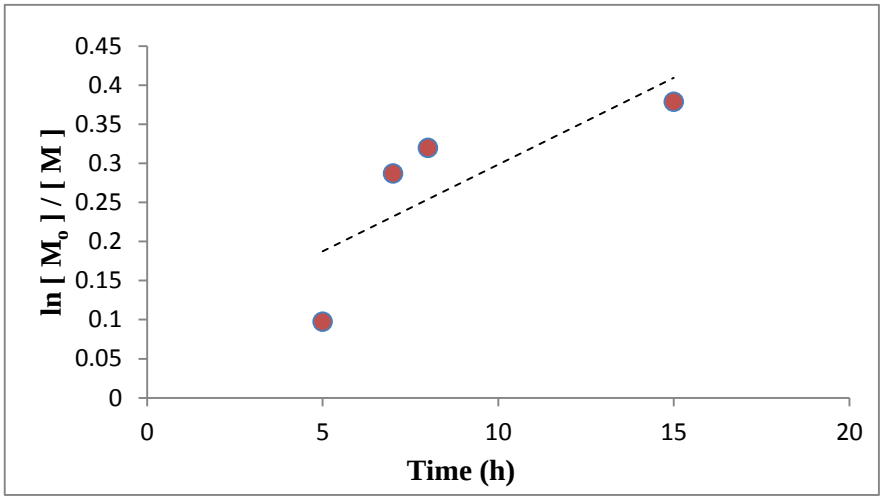


Figure 4.13: Synthesis of pMMA with bifunctional initiator CBD-Br.

Figure 4.14 shows, the semi-logarithmic kinetic plot of ln([M]$_o$/[M]) versus time, t, where [M]$_o$ is the initial concentration of the monomer, and [M] is the monomer concentration at any time and also plots of Mn and polydispersity indexes (Mw / Mn) as a function of conversion. The linearity of the plot indicates that the concentration of growing radicals is constant. [M]/[I]/[Cu]/[PMDETA] = 200/1/4/8, [MMMA]o = 4.64 M for polymerization CBD-Br.



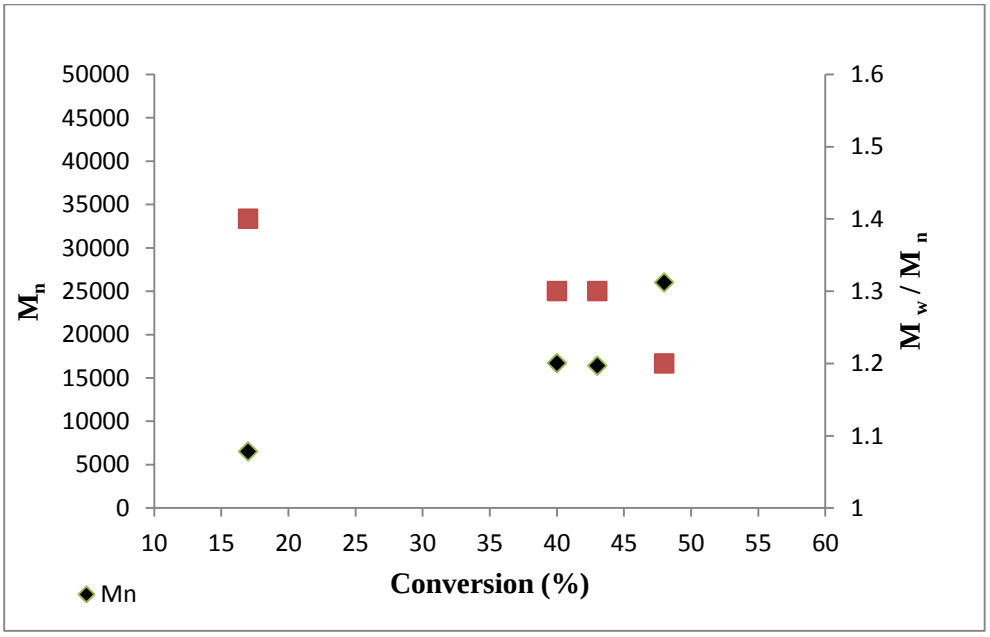


Figure 4.14: First order kinetic plots for polymerization of MMA using CBD-Br as initiator and CuBr as catalyst in anisole at 90 ^oC.

All CBD-pMMAs have the same FT-IR spectra which is shown in Figure 4.13. It can be seen that there was an absorption band from 1145 cm^{-1} to 1240 cm^{-1}, that could be

connected to the C-O-C stretching vibration. α-methyl group vibrations appearance as two bands at 1387 cm^{-1} and 751 cm^{-1}. The band at 984 cm^{-1} was the characteristic absorption vibration of PMMA, together with the bands at 1062 cm^{-1} and 841 cm^{-1}. The band at 1724 cm^{-1} showed the presence of the acrylate carboxyl group. The band at 1434 cm^{-1} could be attributed to the bending vibration of the C-H bonds of the -CH_3 group. The two bands at 2949 cm^{-1} and 2995 cm^{-1} could be assigned to the C-H bond stretching vibrations of the -CH_3 and -CH_2- groups. All of FT-IR spectrums prove that it could be the prepared polymer was indeed macromolecular PMMA [59]. The disappearance of C-Br peak proved that Br functions participated in initiating the PMMA chain growth.

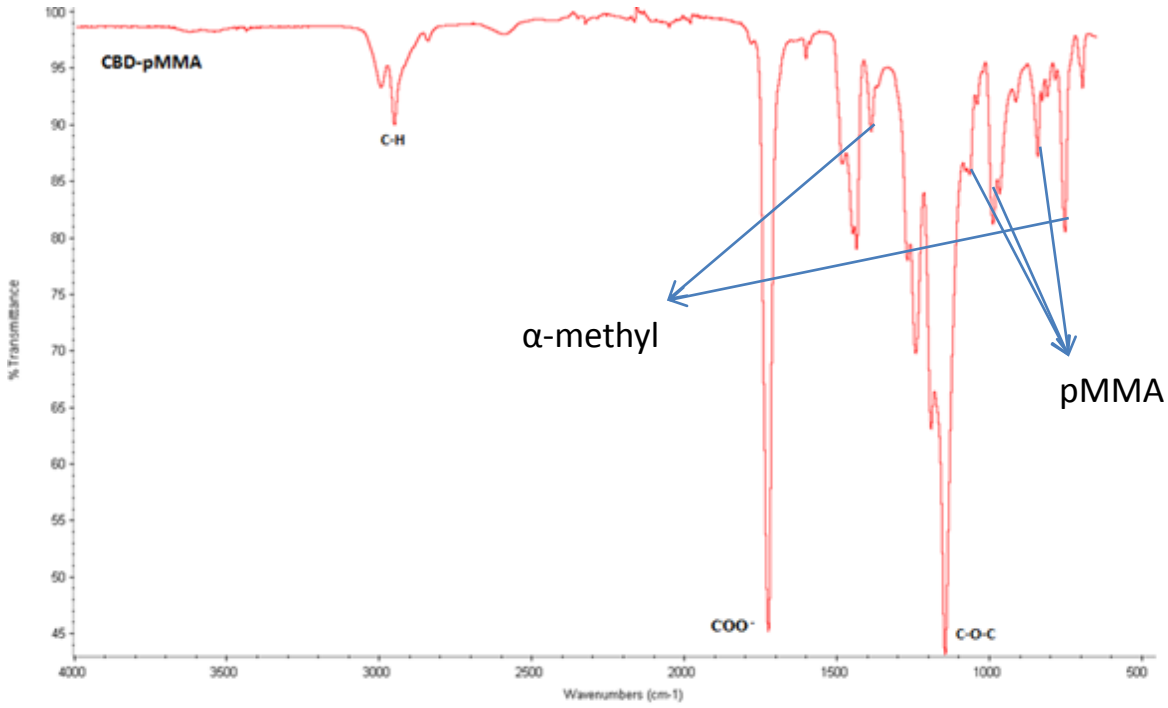


Figure 4.15: FT-IR spectrum of pMMA with bifunctional initiator.

^{1}H-NMR, in addition to the large absorption of the repeat units of PMMA, the characteristic signals were clearly visible Figure 4.16. The ^{1}H-NMR was taken in DMSO-d_6. The complete disappearance of initiator CBD-Br signals indicated that Br functions took part in initiating the PMMA chain growth.

The ^{1}H-NM R spectra of between 0.6 ppm and 1.8 ppm corresponded to the methylene protons of pMMAs, -OCH_2 protons at 3.80 ppm (t,2H), -OCH_3 protons at 3.60 ppm (s,3H) sharp peak comes from pMMAs.

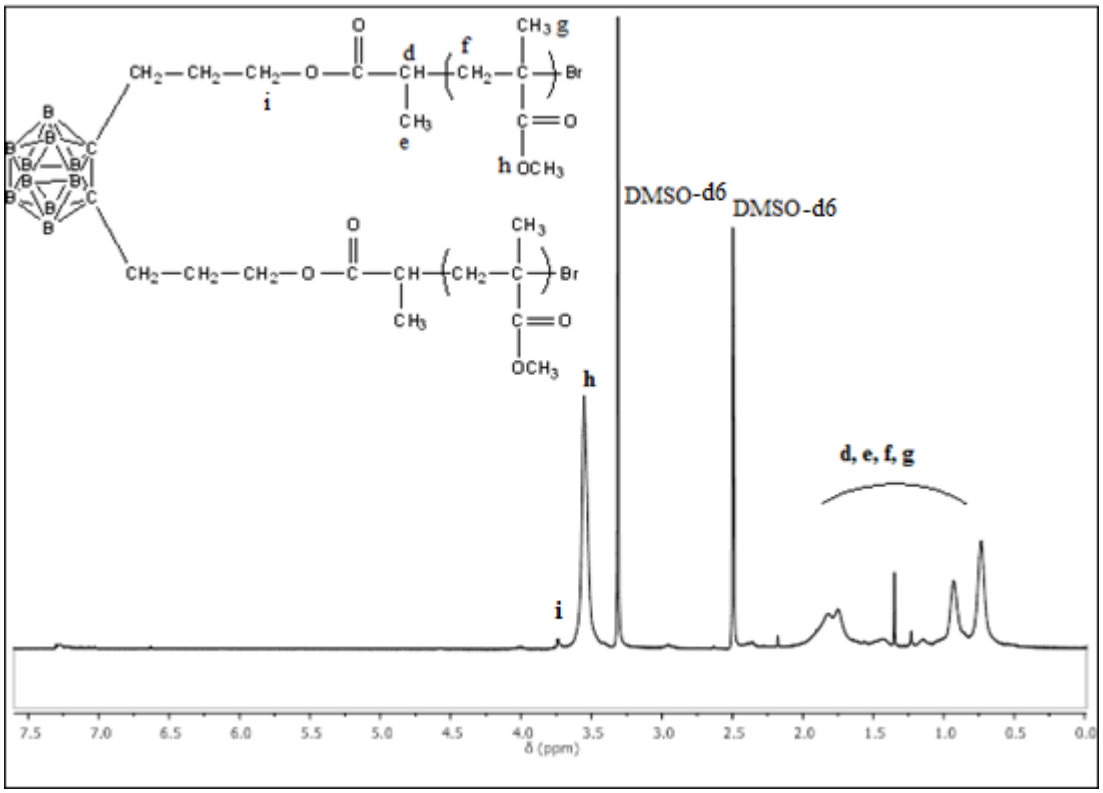


Figure 4.16: ^{1}H-NMR spectrum of CBD-pMMA.

For all bifunctional polymers have same ^{11}B-NMR peaks. In ^{11}B-NMR of CBD-Br as initiator, there is a sharp peak between 0 ppm and -20 ppm. After polymerization was ocuured, the peak remains 25 ppm and -40 ppm moreover it gets broader peaks for the CBD-pMMAs.

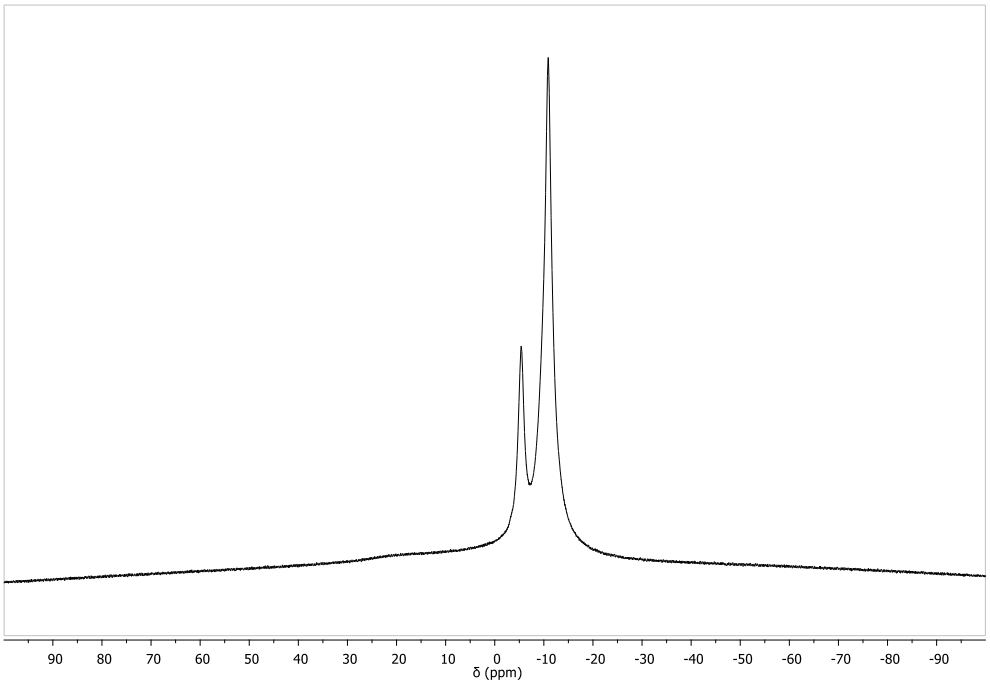


Figure 4.17: ^{11}B-NMR spectrum of CBD-Br.

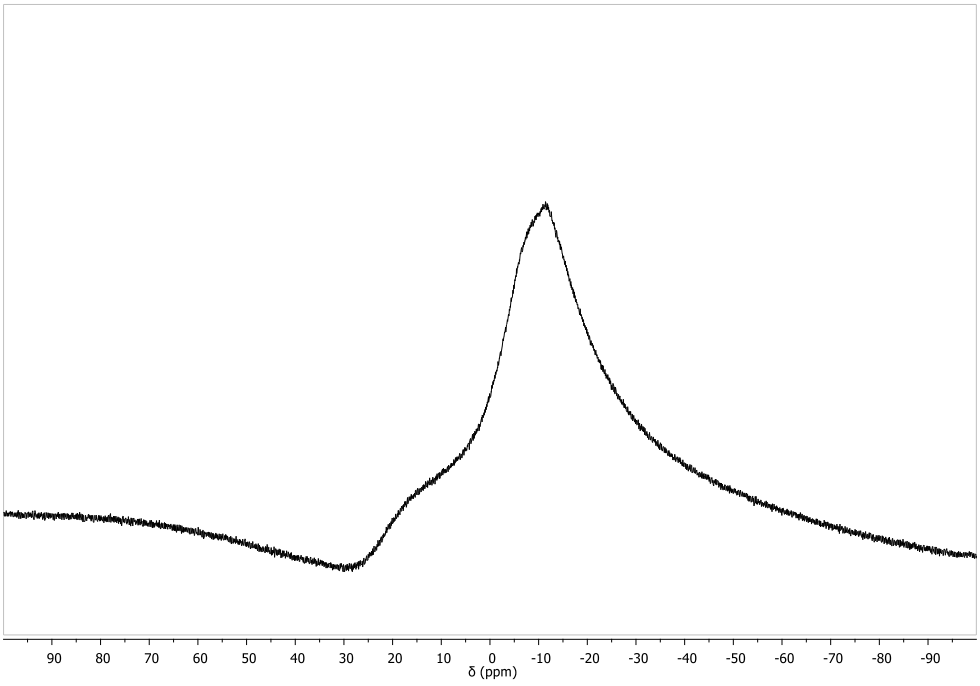


Figure 4.18: ^{11}B-NMR spectrum of CBD-pMMA.

4.4 Thermal Behaviour of PMMA

Thermal behaviours of polymers were examined with DSC and TGA methods. The thermal stability measurements were evaluated by TGA under nitrogen at a heating rate of 20 ^{o}C/min. DSC measurements were conducted with a heating rate of 10^{o}C/min. The results of thermal analysis are shown below tables and figures.

The Tg values of CBM-pMMAs were in the range of 92-118 ^{o}C. The results of all polymers are showed in Table 4.1. and DSC thermogram is showed in Figure 4.19. Therefore; it can be said that the initiator affected T*g* values of all pMMAs. Increasing Tg values corresponded higher moleculer weight of pMMAs.

Table 4.1: DSC results for CBM-pMMA.

Polymer	M_n	T_g(°C)
CBM-pMMA1	4400	92
CBM-pMMA2	12500	99
CBM-pMMA3	17000	96
CBM-pMMA4	23700	117
CBM-pMMA5	45000	118
[a] pMMA (control)	10.550	112

[a] Molecular weight of pMMA (control) is 10.550 g/mol.

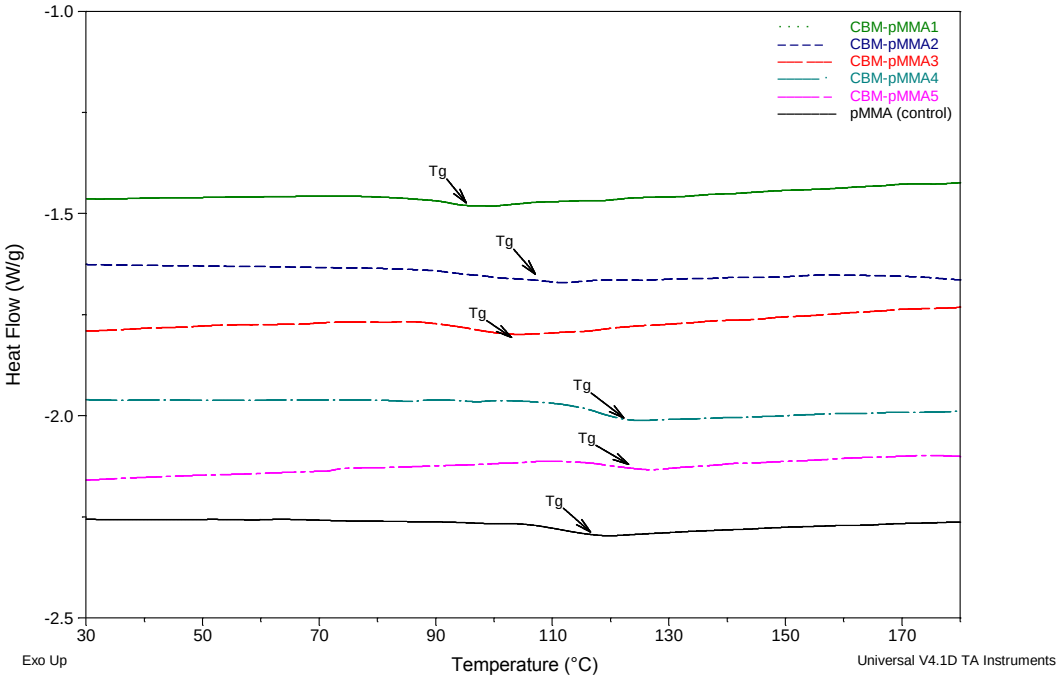


Figure 4.19: DSC thermogram of CBM- pMMAs.

Table 4.2 show the weight loss of CBM-pMMAs in a nitrogen atmosphere as a function of temperature. It can be 50% decomposition temperature decreases depending increases molecular weight of polymers. This results cause smaller residue values that were measured at 500°C/800°C.

Table 4.2: TGA results of CBM-pMMA.

Polymer	$T_{\%50}$ (°C)	Residue at 500°C/800°C (mg)	
CBM-pMMA1	399.3	3.5	1.1
CBM-pMMA2	398.6	0.9	0.2
CBM-pMMA3	374.6	0.7	0.6
CBM-pMMA4	382.2	0.0	0.0
CBM-pMMA5	379.7	3.3	2.8
[a] pMMA (control)	394.9	1.26	0.0

[a] Molecular weight of pMMA (control) is 10.550 g/mol.

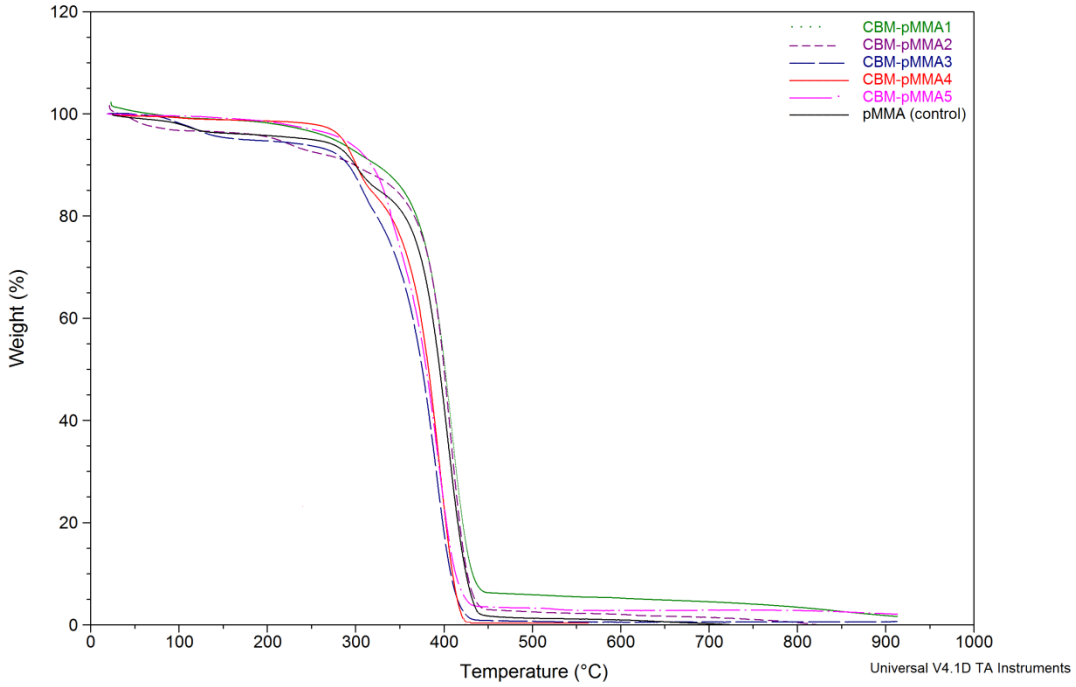


Figure 4.20: TGA thermograms of CBM-pMMAs.

The Tg values of CBD-pMMA were in the range of 92-119 ºC. The results of all polymers are showed in Table 4.3. and DSC thermogram is showed in Figure 4.21.

So; it can be said that the initiator affected T*g* values of all pMMAs. Increasing Tg values corresponded increasing moleculer weight of pMMAs.

Table 4.3: DSC results for CBD-pMMA.

Polymer	M_n	T_g(°C)
CBD-pMMA1	6500	92
CBD-pMMA2	16700	110
CBD-pMMA3	16500	119
CBD-pMMA4	27000	110
[a] pMMA (control)	10.550	112

[a] Molecular weight of pMMA (control) is 10.550 g/mol.

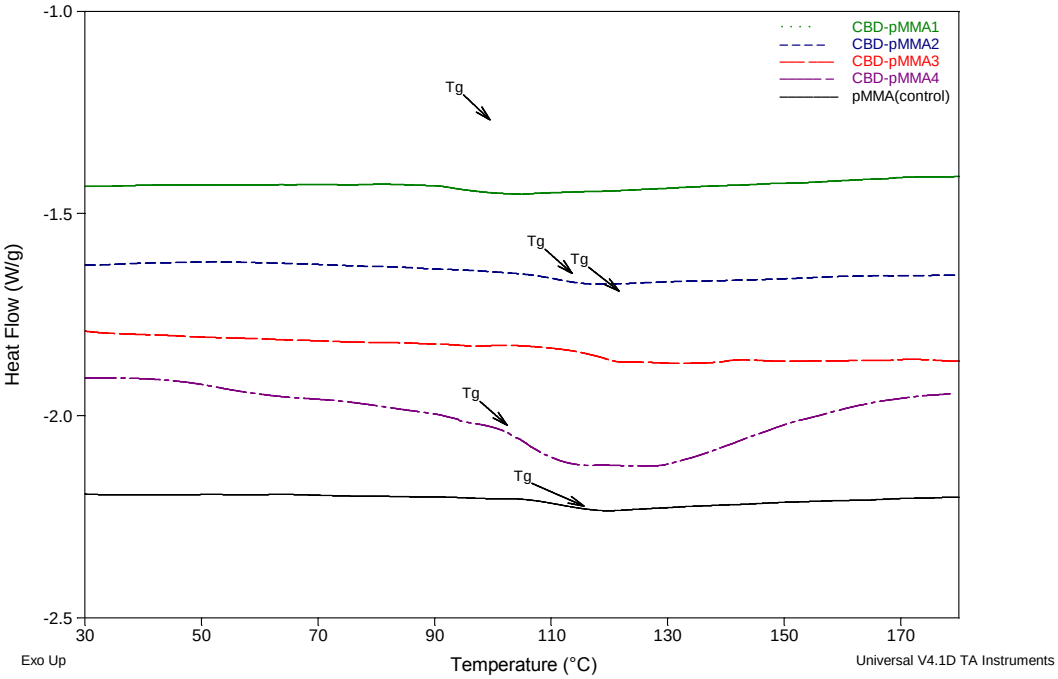


Figure 4.21: DSC thermogram of CBD-pMMAs.

Table 4.4 show the weight loss of CBD-pMMAs in a nitrogen atmosphere as a function of temperature. It can be 50% decomposition temperature increases depending increases molecular weight of polymers. This results cause smaller residue values that were measured at 500°C/800°C.

Table 4.4: TGA results of CBD-pMMA.

Polymer	$T_{\%50}$ (°C)	Residue at 500°C/800°C (mg)	
CBD-pMMA1	382.9	0.0	0.0
CBD–pMMA2	387.3	1.9	0.0
CBD–pMMA3	390.1	2.9	2.9
CBD–pMMA4	402.4	2.4	2.0
[a] pMMA (control)	394.9	1.3	0.0

[a] Molecular weight of pMMA (control) is 10.550 g/mol.

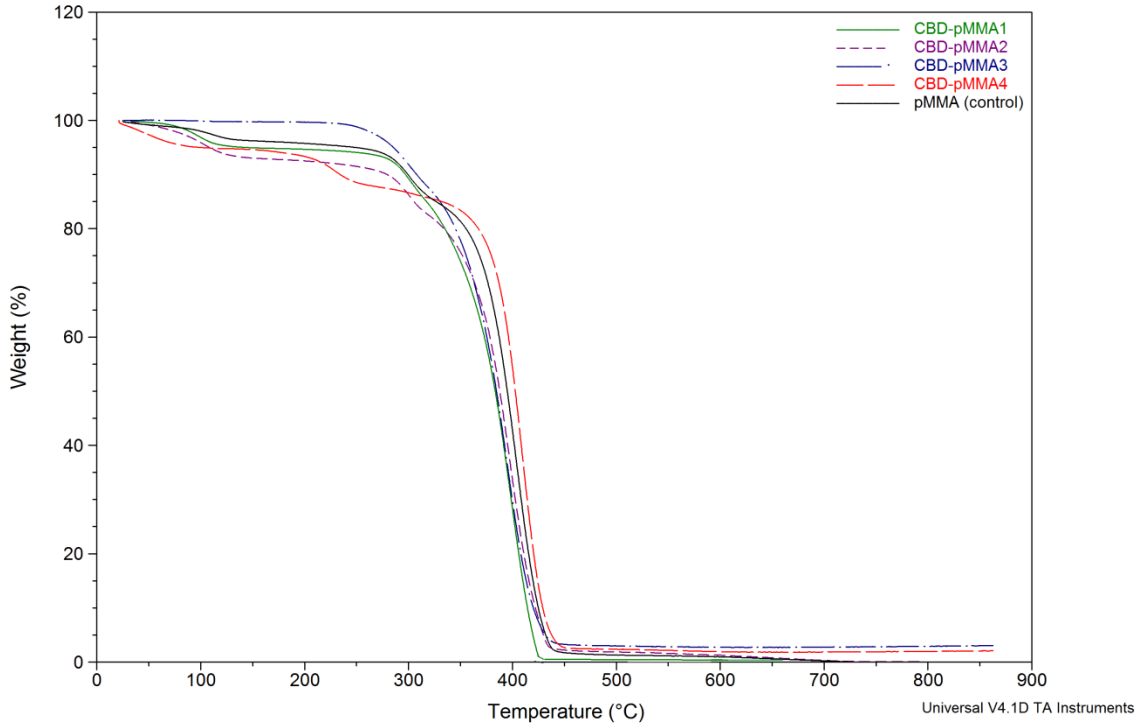


Figure 4.22: TGA thermograms of CBD-pMMAs.

5.CONCLUSION

The aim of this study is to synthesize monofunctional and bifunctional alkynyl-substituted *o*-carborane and use them as initiators to have one and two armed polymers. In this study, new ATRP initiators, CBM-Br and CBD-Br, having active bromine group were synthesized and used to perform ATRP of methylmethacrylate (MMA) in the presence of CuBr/PMDETA. Characterization of the initiator and polymers were thoroughly performed and confirmed by using ^{1}H-NMR, ^{11}B-NMR and FT-IR spectroscopy. Synthesized pMMAs had relatively narrow molecular weight distrubition. A linear relationships between both $\ln[M]_o/[M]$ vs. time and molecular weight vs. conversion indicated controlled/ living polymerization of MMA using CBM-Br and CBD-Br as ATRP initiator. The DSC results of both CBM-pMMAs and CBD-pMMAs are correlate well with the results of pMMA (control) polymer. Tg values of all polymers increases with the molecular weight of polymers. TGA analysis of polymers which have both CBM-Br and CBD-Br as an initiators were calculated and carboranes as core into the polymer did not change residue amount in TGA analysis much.

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